ИЗВЕСТИЯ
АКАДЕМИИ НАУК СССР
ОТДЕЛЕНИЕ
ХИМИЧЕСКИХ НАУК

BULLETIN OF THE ACADEMY OF SCIENCES

OF THE USSR

Division of Chemical Science

(IZVESTIYA AKADEMY NAUK SSSR)
(OTDELENIE KHIMICHESKIKH)

IN ENGLISH TRANSLATION

1955

INDEX

CONSULTANTS BUREAU, INC.
227 WEST 17TH STREET, NEW YORK 11, N. Y.
an agency for the interpretation of international knowledge

SOVIET RESEARCH
in
CATALYSIS

Chemistry Collection No. 3. Covers all aspects of catalysis; papers selected from all Soviet chemical journals translated by Consultants Bureau, 1949-1955.

Sections may be purchased separately as follows:

I.	Theoretical and Sundry Associated Effects	262 pages	$50.-	
IIa.	General	250 pages	50.-	$125.-
IIb.	General	250 pages	50.-	
IIc.	General: Reduction-Oxidation and Fischer-Tropsch	214 pages	50.-	
III.	Hydrogenation Dehydrogenation Cracking	194 pages	50.-	
IV.	Isomerization Alkylation Dehydration	174 pages		$50.-
V.	Polymerization Friedel-Crafts Zeigler	128 pages		30.-

The Collection, comprising 1,672 pages, 262 papers may be purchased as a unit for $200.00

Individual papers are available separately – Table of Contents on request.

CONSULTANTS BUREAU, INC.

227 WEST 17TH STREET, NEW YORK 11, N. Y.

BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR
DIVISION OF CHEMICAL SCIENCES

1955

Index

Publication of the Academy of Sciences of the U.S.S.R.

IN ENGLISH TRANSLATION

Copyright, 1958

CONSULTANTS BUREAU, INC.
227 West 17th Street
New York 11, N. Y.

Printed in the United States

Annual subscription $80.00
Index $ 5.00

SECTIONS

Page

Table of Contents, 1955 1
Author Index, 1955 12
Subject Index, 1955 21

Any of the articles listed herein may be purchased separately, exactly as they appear in the published translation, for $7.50. Individual issues may be purchased for $20.00 each. The price of the translation of the entire volume is $80.00.

When ordering articles, please cite the pagination of the English translation. Direct your orders to:

CONSULTANTS BUREAU, INC.

227 West 17th Street

New York 11, N. Y.

TABLE OF CONTENTS

1955

January-February 1955

	Page	Russ. page
Field of Solid Solutions Formed by Celsian, Dibarium Trisilicate, and Barium Disilicate (Sanbornite). N. A. Toropov, F. Ya. Galakhov, and I. A. Bondar	1	3
Adsorption of Vapor at a Mercury Surface. Communication 1. B. P. Bering and K. A. Ioileva	7	9
Systems Containing Hydrogen Peroxide at High Concentration. Communication 7. 0° Isotherm of the Ternary System NaOH − H_2O_2 − H_2O. S. Z. Makarov and N. K. Grigoryeva	15	17
Babinet's Principle, and the Low-Angle Scattering of X-Rays by Porous Glasses. E. A. Porai-Koshits and V. N. Filipovich	19	21
Structure of Sodium Borosilicate Glasses in Its Relation to The Phenomenon of Opalescence. Communication 1. Investigation of the Opalescence of Glasses. D. L. Levin, S. P. Zhdanov, and E. A. Porai-Koshits	27	31
Preparation of Carboxylic Acids of Structure $CCl_3(CH_2)_nCOOH$ and $CCl_2{=}CH(CH_2)_nCOOH$, and Their Dissociation Constants. A. N. Nesmeyanov, L. I. Zakharkin, and R. Kh. Freidlina	35	40
Reactions of Organomagnesium Compounds with Potassium and Triethyloxonium Fluoborates. A. N. Nesmeyanov, V. A. Sazonova, G. S. Liberman, and L. I. Emelyanova	41	48
Reactions of Mercapto Amino Acids. Communication 1. 3,3-Dimethylisocysteine and Its Derivatives. I. L. Knunyants, M. G. Linkova, and P. G. Ignatenok	47	54
Reactions of Mercapto Amino Acids. Communication 2. Acylation and Alkylation of 3,3-Dimethylcysteine. I. L. Knunyants and M. G. Linkova	53	62
Reactions of Mercapto Amino Acids. Communication 3. Acylation and Alkylation of 3,3-Dimethylcysteine. I. L. Knunyants, O. V. Kildisheva, and M. G. Linkova	61	71
Stereochemistry of Cyclic Compounds. Communication 4. Condensation of 1-Vinylcyclohexene with Citraconic Anhydride. I. N. Nazarov, V. F. Kucherov, and V. M. Andreev	67	78
Stereochemistry of Cyclic Compounds. Communication 5. Condensation of 1-Vinylcyclohexene with Dimethyl Mesaconate. I. N. Nazarov, V. F. Kucherov, and V. M. Andreev	77	89
Theory of Tautomeric Equilibrium in Solution. Effect of Solvation on the Equilibrium Between The Keto and Isomeric Cis and Trans Enol Forms. M. I. Kabachnik	85	98
High-Temperature Contact-Catalysis Reactions of Benzene and Its Closest Homologs in Presence of Hydrogen at High Pressure. N. I. Shuikin and N. G. Berdnikova	95	109
Synthesis of Esters of Polyvinyl Alcohol. S. N. Ushakov and T. A. Kononova	103	117
Reactions of Unsaturated and Macromolecular Compounds, Communication 4. Copolymerization of Some Vinyl Compounds with 2-Vinyloxyethanol. M. F. Shostakovsky and A. M. Khomutov	109	126
Reactions of Unsaturated and Macromolecular Compounds. Communication 5. Copolymerization of Methyl Acrylate with Vinyl Ethers. M. F. Shostakovsky and A. M. Khomutov	115	133

	Page	Russ. page
Polymerization of Vinyl Compounds. Communication 1. Stepwise Synthesis of Poly[Butyl Vinyl Ether]. M. F. Shostakovsky and V. A. Gladyshevskaya	121	140
Synthesis and Reactions of Vinyl Ethers of Ethanolamines. Communication 6. Vinyl Ether of 2-Anilinoethanol. M. F. Shostakovsky and I. A. Chekulaeva	127	146
Synthesis of Sulfur Compounds by the Aid of Vinyl Ethers and Acetylene. Communication 11. Ion-Catalyzed Reactions of Ethyl Vinyl Sulfide. M. F. Shostakovsky, E. N. Prilezhaeva, and N. I. Uvarova	135	154
Macromolecular Compounds. Communication 69. Dependence of the Properties of Polyamides on the Extent of Intermolecular Hydrogen Bonding. V. V. Korshak and T. M. Frunze	143	163
Macromolecular Compounds. Communication 70. Peculiar Features of Chain Growth During Polycondensation in Presence of a Catalyst. G. S. Kolesnikov, V. V. Korshak, and T. V. Smirnova	151	172

Brief Communications

	Page	Russ. page
2-Aminovinyl Ketones. Communication 3. Synthesis of Alkyl 2-Aminovinyl Ketones. A. N. Nesmeyanov, N. K. Kochetkov, and Ya. V. Dombrovsky	157	179
Reaction of 3-Buten-1-ynylmagnesium Bromide with Halotriphenylsilanes. A. D. Petrov, S. I. Sadykhzade, and V. M. Vdovin	159	181
Synthesis of 3- and 5-Alkenyltrialkylsilanes. V. F. Mironov and N. A. Pogonkina	161	182
Synthesis of Sodium Tetraphenylboron. A. N. Nesmeyanov and V. A. Sazonova	166	187

March-April 1955

	Page	Russ. page
Crystal-Optical Method for Determining the Structure of Complex Compounds. G. B. Boky and S. S. Battanov	173	193
Structure of Sodium Borosilicate Glasses in Its Relation to the Phenomenon of Opalescence. Communication 2. Investigation of the Structure of Porous Glasses. S. P. Zhdanov, E. A. Porai-Koshits, and D. I. Levin	177	197
Systems Containing Hydrogen Peroxide at High Concentration. Communication 8. Thermal Characteristics and Stabilities of Solid Phases of the System $NaOH - H_2O_2 - H_2O$. S. Z. Makarov and N. K. Grigoryeva	187	208
Adsorption of Vapor at a Mercury Surface. Communication 2. B. P. Bering and K. A. Ioileva	193	216
ω-Chloro Carboxylic Acids, and Some of Their Reactions. A. K. Nesmeyanov and L. I. Zakharkin	199	224
Chlorination and Dehydrochlorination of Polychloro Compounds Containing Reactive Groups. R. Kh. Freidlina, V. N. Kost, and A. N. Nesmeyanov	207	233
Derivatives of Unsaturated Phosphonic Acids. Communication 5. Esters of 2-Ethoxy-, 2-Propoxy-, 2-Butoxy-, and 2-Hexyloxyvinylphosphonic Acids. K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov	213	240
The Products of the Action of Sodium Diethyl Phosphorothionate on Alkyl Phosphorodichloridites. B. A. Arbuzov and P. I. Alimov	221	249

	Page	Russ. page
Esters of Ethylphosphonous Acid and Some of Their Reactions. Communication 5. Synthesis of Esters of Dialkylphosphinic Acids. B. A. Arbuzov and N. I. Rizpolozhensky	225	253
Reactions of Mercapto Amino Acids. Communication 4. N-Acyl-2,3-dihaloalanines. O. V. Kildisheva, L. P. Rasteikene and I. L. Knunyants	231	260
Reactions of Mercapto Amino Acids. Communication 5. N-Acyl-3-halo-2-hydroxyalanines and Their Derivatives. O. V. Kildisheva, M. G. Linkova, and I. L. Knunyants	241	271
Reactions of Mercapto Amino Acids. Communication 6. 2-(Acylamino)-3-haloacrylic Acids and Their Derivatives. O. V. Kildisheva, M. G. Linkova, and I. L. Knunyants	251	282
Stereochemistry of Cyclic Compounds. Communication 6. Lactonization of cis- and trans- 1,2,3,5,6,7,8,8a-Octahydro-1,2-naphthalenedicarboxylic Acids. I. N. Nazarov, V. F. Kucherov, and V. M. Andreev	257	289
Stereochemistry of Cyclic Compounds. Communication 7. Geometric Isomerism of 4-Methyl-1,2-cyclohexanedicarboxylic Acids. I. N. Nazarov and V. F. Kucherov . . .	265	298
Catalytic Amination of Alcohols. M. A. Popov and N. I. Shuikin	275	308
Reactions of Individual Hydrocarbons in Contact with Natural Aluminosilicates. Communication 3. Reactions of Cyclopentane, Ethylcyclopentane, Ethylcyclohexane, and Ethylbenzene in Presence of Troshkov Clay. N. I. Shuikin and E. A. Timofeeva	281	314
Photodehydrocondensation of Anisole Homologs, Photosynthesis of Synestrol. B. M. Mikhailov and A. N. Blokhina	289	323
Absorption Spectra and Molecular Structure. Communication 3. Modern Electronic Theory, and the Color of Arylhydrazones of 9-Acridinecarboxaldehyde. A. A. Kharkharov	293	326
Some Physico-Mechanical Properties of Esters of Polyvinyl Alcohol. S. N. Ushakov and T. A. Kononova	301	335
Polymerization of Vinyl Compounds. Communication 2. Stepwise Synthesis of Poly [Ethyl Vinyl Ether]. M. F. Shostakovsky and V. A. Gladyshevskaya	309	344
Reactions between Vinyl Compounds and Multifunctional Compounds. Communication 4. Reaction of Alkyl Vinyl Ethers with Glycerol and with Glycerol 1,2-and 1,3-Cyclic Acetals. M. F. Shostakovsky, V. V. Zhebrovsky, and M. A. Medelyanovskaya	313	350
Reaction Between Vinyl Compounds and Multifunctional Compounds. Communication 5. Reaction of Glycerol Trivinyl Ester with Monohydric Alcohols. M. F. Shostakovsky, V. V. Zhebrovsky, and M. A. Medelyanovskaya.	317	354
Macromolecular Compounds. Communication 71. Polycondensation of 1,2-Chloroethane with Chlorobenzene in Presence of Aluminum Chloride. G. S. Kolesnikov, V. V. Korshak. and L. S. Fedorova	321	359
Macromolecular Compounds Communication 72. Formation of a Three-Dimensional Polymer by Reaction of Poly[ethylenephenyl] with Dihaloalkanes. V. V. Korshak, G. S. Kolesnikov, and T. A. Soboleva	327	365
Macromolecular Compounds. Communication 73. Some Two-Component Mixed Polyamides. V. V. Korshak and T. M. Frunze	333	372

Brief Communications

	Page	Russ. Page
Reaction of 2-Methylallylmagnesium Chloride with Esters of Palmitic and 2-Ethylhexanoic Acids. A. D. Petrov, V. M. Melekhin, and O. M. Nefedov	339	380

May-June 1955

General and Inorganic Chemistry

A. V. Dumansky (Salutation on 75th Birthday)	343	None
Experimental Determination of the Sequence of Successive Elementary Reactions of Atoms and Radicals. L. I. Avramenko and R. Kolesnikova	345	386
Structure of Sodium Borosilicate Glasses in its Relation to the Phenomenon of Opalescence. Communication 3. Comparison of the Results of Investigations on Sodium Borosilicate Glasses and on Porous Products Obtained from them by Leaching. E. A. Porai-Koshits, S. P. Zhdanov, and D. I. Levin	353	395
Reaction of Vitreous Sodium Silicates and Aluminosilicates with Aqueous Solutions. Communication 6. Reaction of Vitreous Sodium Silicates and Aluminosilicates with Caustic Alkali Solutions. S. K. Dubrovo and Yu. A. Schmidt	359	403
Systems Containing Hydrogen Peroxide at High Concentration. Communication 9. The Ternary System $LiOH-H_2O_2-H_2O$. S. Z. Makarov and T. A. Dobrynina	365	411
Equation for the Diffusion Current at a Dropping Electrode Taking Into Account the Screening of Part of the Electrode Surface. S. G. Mairanovsky and M. B. Neiman	373	420

Organic and Biological Chemistry

Derivatives of Unsaturated Phosphonic Acids. Communication 6. Diesters of 2-Isopropoxy-, 2-Isobutoxy-, and 2-Isopentyloxy-Vinylphosphonic Acids. K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov	377	425
Derivatives of Unsaturated Phosphonic Acids. Communication 7. Diesters of 2-Phenoxyvinylphosphonic Acid. K.N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov	383	432
Action of Some Alkoxy Compounds on Trialkoxy-and Dialkoxychloro-Stibines. B. A. Arbuzov and O. D. Samoilova	385	435
Synthesis of Chloramphenicol. G. Fodor, J. Toth, E. Kovacs, and J. Kiss	391	441
Reactions of Mercapto Amino Acids. Communication 7. Reactions of N-Acyl-2,3-dihaloalanines and (Acyloxy)Pyruvic Acids. O. V. Kildisheva, M. G. Linkova, and I. L. Knunyants	401	452
Reactions of Mercapto Amino Acids. Communication 8. Alkylation and Acylation of Cysteine and 3,3-Dimethylcysteine by Derivatives of N-Acyl-3-Haloalanines. I. L. Knunyants and V. V. Shokina	409	462
New Method for the Preparation of Primary and Secondary Organoarsenic Compounds. I. L. Knunyants and V. Ya. Pilskaya	417	472
Synthesis of Steroid Compounds and Related Substances. Communication 29. Condensation of Isoprene with 2-Methyl-2-cyclohexen-1-one. Synthesis of cis-1,2,4a,5,8,8a-Hexahydro-4a,7-dimethyl-4-vinylnaphthalene. I. N. Nazarov and G. P. Kugatova	423	480
Stereochemistry of Cyclic Compounds. Communication 8. Condensation of cis-1,2,4a, 5,8,8a-Hexahydro-4a,7-Dimethyl-4-vinylnaphthalene with Citraconic Anhydride. I. N. Nazarov, V. F. Kucherov, and G. P. Kugatova	429	487

	Page	Russ. Page
High-Temperature Reactions of Methylcyclohexane in a Continuous-Flow System in Presence of Metals of the Palladium Group and of Hydrogen at High Pressure. N. I. Shuikin, Kh. M. Minachev, L. M. Feofanova, E. G. Treshchova, T. P. Yudkina, and A. E. Agronomov	441	501
Destructive Alkylation of Benzene with Pentane. I. M. Tolchinsky, B. A. Krentsel, and A. V. Topchiev	451	512
Behavior of 3-,4-,and 5-Alkenyl Halides in Condensation Reactions with Alkyl Halides in Presence of Magnesium. M. A. Cheltsova, E. A. Chernyshev, and A. D. Petrov	459	522
Synthesis of Organosilicon Esters of Propionic and Isobutyric Acids, and Their Properties. D. N. Andreev, B. N. Dolgov, and E. V. Kukharskaya	465	528
Reactions of Epichlorohydrin and of Glycidol with Organochlorosilanes. K. A. Andrianov, N. N. Sokolov, E. N. Khrustaleva, and L. N. Yukina	469	531
Reactions Between Vinyl Compounds and Multifunctional Compounds. Communication 6. Reaction of Vinyl Ethers with Pentaerythritol. M. F. Shostakovsky, A. S. Atavin, and V. V. Zhebrovsky	477	539
Optical Investigation of Some Vinyl Ethers of Ethanolamines. M. F. Shostakovsky, M. I. Batuev, I. A. Chekulaeva, and A. D. Matveeva	481	544
Macromolecular Compounds. Communication 74. Effect of Aromatic Components on the Properties of Mixed Polyamides. V. V. Korshak and T. M. Frunze	487	551
Macromolecular Compounds. Communication 75. Dependence of the Properties of Polyamides on the Extent of Intermolecular Hydrogen Bonding. V. V. Korshak and T. M. Frunze	493	558
Macromolecular Compounds. Communication 76. Role of Exchange Reactions in Polyamide Formation. V. V. Korshak and T. M. Frunze	499	563

Brief Communications

	Page	Russ. Page
Contact-Catalysis Reactions of Pentane in Presence of a Chrome-Alumina-Magnesia Catalyst. N. I. Shuikin, E. A. Timofeeva, and V. M. Sladkikh	503	567
β-Thiolactones. M. G. Linkova, O. V. Kildisheva, and I. L. Knunyants	507	569
Synthesis and Reactions of Some 2,2'-Methylenedithiophene Derivatives. Ya. L. Goldfarb and M. L. Kirmalova	509	570
Relation Between the Mobilities of Ions in Solution and Their Self-Diffusion Coefficients. O. Ya. Samoilov	513	572

July-August 1955

	Page	Russ. Page
Radiochemical Investigation of Spallation and Fission Reaction Products Resulting From the Bombardment of Bismuth with 660-Mev Protons. A. N. Murin, B. K. Preobrazhensky, and N. E. Titov	517	577
Interphase Partition in Systems Containing Anomalous Mixed Crystals. Communication 4. The Systems $NH_4Cl-CuCl_2-H_2O$ and $NH_4Cl-CrCl_3-H_2O$. E. M. Ioffe	525	586
Surface and Sorption Properties of Active Carbons. Communication 1. Sorption Isotherms for Benzene and Water Vapor. M. M. Dubinin and E. D. Zaverina	531	594

	Page	Russ. Page
Reaction of Vitreous Sodium Silicates and Aluminosilicates with Aqueous Solutions. Communication 7. Reaction of Vitreous Sodium Silicates and Aluminosilicates with Salt Solutions. S. K. Dubrovo and Yu. A. Shmidt	539	603
Physicochemical Study of Lithium Peroxide. T. V. Rode, T. A. Dobrynina, and G. A. Golder	545	611
Synthesis of 2,2'-Azobis [2-Methylproprionitrile] Labeled with Radioactive Carbon (C^{14}). M. M. Koton, T. M. Kiseleva, and F. S. Florinsky	555	622
Present State of the Catalysis Problem and the Theoretical Basis of the Search for Catalysts. A. A. Balandin	557	624
Synthesis of Branched Aliphatic Hydrocarbons Via 2-Alkenyl Halides. A. D. Petrov . .	571	639
Some Reactions of Alkyl 2-Phenoxyvinyl Ketones. A. N. Nesmeyanov, N. K. Kochetkov, M. I. Rybinskaya, and E. V. Uglova	579	649
Synthesis of Dodecanedioic and Hexadecanedioic Acids. A. N. Nesmeyanov, L. I. Zakharkin, and T. A. Kost	585	657
Derivatives of Unsaturated Phosphonic Acids. Communication 8. Bisdialkylamides of 2-Alkoxy- and 2-Phenoxy-Vinylphosphonic Acids. K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov	591	665
Derivatives of Unsaturated Phosphonic Acids. Communication 9. Diesters of 2-Alkoxy-and 2-Phenoxy-Vinylphosphonothionic Acids. K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov	595	669
Some Esters of Phosphorodithioic Acid as Insecticides. B. A. Arbuzov, K. V. Nikonorov, and G. M. Vinokurova	597	671
Action of Halogens on Esters of Antimonous Acid. B. A. Arbuzov and O. D. Samoilova.	601	676
Synthesis of Phosphonic Esters Containing Heterocyclic Radicals. Communication 5. Phosphonic Esters Containing A Hydrocoumarin Radical. B. A. Arbuzov and V. M. Zoroastrova	605	681
Reactions of Mercapto Amino Acids. Communication 9. Synthesis of α- Acylamino β-Thiolactones. I. L. Knunyants, O. V. Kildisheva, and E. Ya. Pervova	613	689
Reactions of Mercapto Amino Acids. Communication 10. New Method for the Synthesis of Polypeptides. I. L. Knunyants, O.V. Kildisheva, and E. Ya. Pervova.	619	696
Addition Reactions of Perfluoroolefins. Communication 3. Addition of Sulfur Chlorides. I. L. Knunyants and A. V. Fokin	627	705
Dearylation of Ar_2PbX_2 as a Method of Synthesizing a New Class of Compounds $ArPbX_3$. K. A. Kocheshkov and E. M. Panov	633	711
Compounds of the Classes Ar_2PbX_2 and $ArPbX_3$ in the p-Tolyl Series. K. A. Kocheshkov and E. M. Panov	639	718
Free Energy in the Adsorptional Displacement of Butene by Water From a Catalyst Surface. A. A. Balandino, O. K. Bogdanova, and A. P. Shcheglova	643	723
Synthesis of Sulfur Compounds by the Aid of Vinyl Ethers and Acetylene. Communication 12. The Most Effective Catalysts for the Addition of Hydrogen Sulfide to Vinyl Ethers in the Direction Contrary to Markovnikov's Rule. M. F. Shostakovsky, E. N. Prilezhaeva, and E. S. Shapiro	653	734

	Page	Russ. Page
Synthesis of tert-Butyl Hydroperoxide and tert-Butyl Peroxide, and their Optical Investigation in Relation to the Problem of the Structure of Hydrogen Peroxide. A. P. Meshcheryakov, M. I. Batuev, and A. D. Matveeva	661	742
Exchange and Cleavage Reactions of Quaternary Ammonium Salts. Communication 9. Reaction of Quaternary Ammonium Salts of the Type $[R-O-CH_2-N-]X$ with Secondary and Tertiary Alcohols. V. N. Setkina, N. K. Baranetskaya, and D. N. Kursanov	667	750
Macromolecular Compounds. Communication 77. Dependence of the Properties of Aliphatic Polyamides Having "Even" Repeating Units on the Structure of the Repeating Unit. V. V. Korshak and T. M. Frunze	673	756
Macromolecular Compounds. Communication 78. Dependence of the Properties of Aliphatic Polyamides Having "Odd" Repeating Units on the Structure of the Repeating Unit. V. V. Korshak and T. M. Frunze	679	762

Brief Communications

	Page	Russ. Page
Catalytic Inertness of Amorphous Nickel in the Hydrogenation of Benzene and the Dehydrogenation of Cylcohexane. A. M. Rubinstein, L. Kh. Freidlin, and N. V. Borunova	683	766
Cyanoethylation of Organosilicon Amines. V. F. Mironov, A. D. Petrov, and N. A. Pogonkina	685	768
Effect of the Structural Factor on the Catalytic Decomposition of Alcohols Varying in Molecular Weight. A. M. Rubinshtein and N. A. Pribytkova	689	770
Quantitative Determination of 2,5-Piperazinediones in the Products of the Polycondensation of Esters of α-Amino Acids. K. T. Poroshin, T. D. Kozarenko, and Yu. I. Khurgin	693	773

Current Events

	Page	Russ. Page
General Meeting of the Division of Chemical Sciences of the Academy of Sciences of the USSR	697	775

September-October 1955

	Page	Russ. Page
Systems Containing Hydrogen Peroxide at High Concentration. Communication 10. Thermal Stability of Urea Perhydrate S. Z. Makarov and B. A. Lebedev	705	785
Study, With the Aid of Labeled Atoms, of the Reaction Mechanism of the Oxidation of Methane. Mechanism of the Formation of Carbon Monoxide. I. N. Antonova, V. A. Kuzmin, R. I. Moshkina, A. B. Nalbandyan, M. B. Neiman, and G. I. Feklisov	711	789
Physicochemical Basis of the Formation of Diffusional Surface Layers on Iron and its Alloys. N. S. Gorbunov	715	793
Determination of the Crystallization Coefficient for the Distribution of a Thorium B (Radioactive Lead) Salt Between a Salt Melt and Crystals of an Isomorphous Salt. V. R. Klokman, V. K. Zinovyeva, and L. A. Tseveleva	721	800
Role of Dissociational Activation in the Sintering of Oxides of Elements of Variable Valency. A. I. Leonov.	725	805

	Page	Russ. Page
Reaction of Alkyl 2-Chlorovinyl Ketones with Ethyl Acetoacetate. N. K. Kochetkov, L. I. Kudryashov, and A. N. Nesmeyanov	729	809
Reaction of 2-Chlorovinyl Ketones with Anthracene. A. N. Nesmeyanov, M. I. Rybinskaya, and N. K. Kochetkov	735	817
Derivatives of Unsaturated Phosphonic Acids. Communication 10. Diesters of 2-Alkoxy-and 2-Phenoxy-Vinylphosphonodithiolic and of 2-Alkoxy-and 2-Phenoxy-Vinylphosphonotrithioic Acids. K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov	741	823
Derivatives of Unsaturated Phosphonic Acids. Communication 11. Diesters of 2-(2-Alkoxyethoxy)Vinylphosphonic Acids. K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov	745	827
Derivatives of Unsaturated Phosphonic Acids. Communication 12. Bisdialkylamides of 2-(2-Alkoxyethoxy)vinylphosphonic Acids. K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov	751	834
Synthesis of Alkoxybromotitaniums and Alkoxychloropolytitanoxanes. A. N. Nesmeyanov, E. M. Brainina, and R. Kh. Freidlina.	755	838
Some Derivatives of 1-Hydroxyalkylphosphonic Acids. P. I. Alimov and O. N. Fedorova.	761	844
Addition Reactions of Perfluoroolefins. Communication 4. Reaction of Vinylidene Fluoride with Sulfur Chlorides and with Alkanesulfenyl Chlorides. I. L. Knunyants and E. G. Vykhovskaya	769	852
Complex Nature of Dimetal Compounds of Phenazine. B. M. Mikhailov and A. N. Blokhina	775	859
Catalytic Hydrogenation of Doubly Unsaturated Compounds Having a Conjugated System of Double Bonds. Communication 3. Hydrogenation of 2,3-Dimethyl-1,3-Butadiene in Presence of Platinum, Nickel, and Palladium. I. V. Gostunskaya, G. V. Loza, and B. A. Kazansky	779	863
Catalytic Dehydrocyclization of Piperylene. N. I. Shuikin and V. A. Tulupov.	785	869
Absorption Spectra and Molecular Structure. Communication 4. Effect of the Character of the Substituent on Color in Derivatives of 9-Acridinecarboxaldehyde Phenylhydrazone Hydrochloride. A. A. Kharkharov	795	880
Identification of Hydrocarbons with the Aid of Dispersion Curves. I. V. Obreimov and T. N. Shkurina	805	890
Comparative Study of the Oxidation Reactions of Pectic Substances, of Cellulose, and of the Structural Units of These Substances. Communication 2. Oxidative Degradation of Sodium Polygalacturonate by Means of Molecular Oxygen Sodium Metaperiodate, and Hydrogen Peroxide. O. P. Golova and N. S. Mayat.	815	899
Synthesis of Sulfur Compounds by the Aid of Vinyl Ethers and Acetylene. Communication 13. General Method for the Synthesis of Vinyl Sulfides. M. F. Shostakovsky, E. N. Prilezhaeva, and N. I. Uvarova	821	906
Synthesis and Reactions of Vinyl Ethers of Ethanolamines. Communication 7. Vinyl Ether of 2-Diphenylaminoethanol. M. F. Shostakovsky and I. A. Chekulaeva.	829	913
Reactions of Unsaturated and Macromolecular Compounds. Communication 6. Copolymerization of Vinylcaprolactam with Methyl Methacrylate in Presence of Benzoyl Peroxide and of 2,2'-Azobis[2-Methylpropionitrile]. M. F. Shostakovsky, F. P. Sidelkovskaya and A. M. Khomutov	835	919

Page | Russ. Page

Macromolecular Compounds. Communication 79. Products of the Polycondensation of Dialdehydes and Diketones with Diamines and Glycols. V. V. Korshak and S. V. Vinogradova 841 925

Macromolecular Compounds. Communication 80. A Case of Migrational Copolymerization. V. V. Korshak and S. V. Vinogradova. 845 930

Macromolecular Compounds. Communication 81. Mixed Polyamides Containing Glutaric or Pimelic Acid Residues. V. V. Korshak and T. M. Frunze 849 934

Macromolecular Compounds. Communication 82. 2,4,5-Triisopropyl-α-Methyl styrene. V. V. Korshak and N. G. Matveeva. 855 942

Brief Communications

Preparation of p-Terphenyl. B. M. Mikhailov and P. M. Aronovich 857 945

Organoboron Compounds. Communication 3. Preparation of the Isobutyl Esters of Phenylpropyl-and Butylphenyl-Borinic Acids. B. M. Mikhailov and P. M. Aronovich 859 946

Synthesis of 1,1-Dichlorosilacyclopent-3-ene. A. D. Petrov, G. I. Nikishin, N. P. Smetankina, and Yu. P. Egorov. 861 947

Reactions of 2-Bromoethyl Phenyl Ether in Presence of Zinc Chloride and a Mixture of Zinc and Aluminum Chlorides. E. N. Karaulova and G. D. Galpern 865 949

Chlorination of Dodecane. V. A. Nekrasova and N. I. Shuikin 867 950

Catalytic Dehydrogenation of Isopentane. N. I. Shuikin, T. P. Dobrynina, E. A. Timofeeva, and Yu. P. Egorov 869 952

Synthesis and Reactions of Oxygen-Containing Organosilicon Compounds. Communication 2. Reactions of Diethyl-and Diphenyl-Silanediols with Vinyl Ethers. M. F. Shostakovsky, D. A. Kochkin, and V. M. Rog. 871 953

OBITUARY, Aleksandr Vasilyevich Trofimov 875 956

November-December 1955

Effect of the Method of Making Modifying Additions on the Properties of Oxide Catalysts. G. M. Zhabrova and E. A. Fokina 879 963

Solid Solutions of Calcium Aluminoferrites. N. A. Toropov and A. I. Boikova 885 972

Kinetics of Bromine Exchange in Complex Platinum Bromides. A. A. Grinberg and G. A. Shagisultanova 895 981

Reactions of Fenchone with Organomagnesium and Organolithium Compounds . A. N. Nesmeyanov, V. A. Sazonova, and R. B. Materikova 901 988

Condensation of 3,3,3-Trichloropropene with Aromatic Compounds. A. N. Nesmeyanov, R. Kh. Freidlina, and N. A. Semenov 905 993

Derivatives of Unsaturated Phosphonic Acids. Communication 13. Diesters of 2-(2-Alkoxyethoxy)Vinylphosphono-Mono-, -Di-, and-Tri-Thioic Acids. K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov 911 999

Derivatives of Unsaturated Phosphonic Acids. Communication 14. Diesters of Styrylphosphonic Acid. K. N. Anisimov and A. N. Nesmeyanov 915 1003

	Page	Russ. Page
Derivatives of Unsaturated Phosphonic Acids. Communication 15. Diesters of β-Chlorostyrylphosphonic and Phenylethynylphosphonic Acids. K. N. Anisimov and A. N. Nesmeyanov	919	1006
Action of Sodium on Compounds Containing a $CCl_2 = CH$ Group. L. I. Zakharkin	923	1009
Synthesis of Alkyl Bis [1-(Diethoxyphosphinyl Alkyl] Phosphites. P. I. Alimov and I. V. Cheplanova	929	1015
Esters of Ethylphosphonous Acid, and Some of Their Reactions. Communication 6. Triethylphosphonamidous Esters. B. A. Arbuzov, N. I. Rizpolozhensky, and M. A. Zvereva	935	1021
Parachors of Trialkylmethylsilanes. B. A. Arbuzov and V. S. Vinogradova	945	1031
New Method of Preparing β-Lactams. I. L. Knunyants and N. P. Gambaryan	951	1037
Acylation of Aminoalkylphosphonic and Aminoalkylphosphonothioic Acids. T. Ya. Medved and M. I. Kabachnik	957	1043
Methylation of 1-Aminoalkylphosphonic Acids and Their Esters. T. Ya. Medved and M. I. Kabachnik	961	1048
Reforming of Tuimazin Gasoline in Contact with Troshkov Kaolin. N. I. Shuikin and E. A. Timofeeva	965	1053
Reactions of 3,3,4-Trimethyl-2-Pentanol. A. P. Meshcheryakov and L. V. Petrova	969	1057
Reactions of Symmetrical Aromatic Mercury Compounds with Phenols. M. M. Koton and V. F. Martynova	975	1063
Absorption Spectra and Molecular Structure. Communication 5. Spectroscopic Investigations of Solutions of Chlorine-Substituted Phenylhydrazones of 9-Acridinecarboxaldehyde Hydrochloride in Alcoholic Hydrogen Chloride. A. A. Kharkharov	983	1071
Comparative Study of the Oxidation Reactions of Pectic Substances, of Cellulose, and of the Structural Units of These Substances. Communication 3. Comparative Study of the Reactivities of the Structural Units of Cellulose and Pectic Substances in Oxidation Reactions with Sodium Metaperiodate and Hydrogen Peroxide. O. P. Golova and N. S. Mayat	991	1078
Polymerization of Isopropyl Vinyl and Cyclohexyl Vinyl Ethers in Presence of 2,2-Azobis [2-Methylproprionitrile]. M. F. Shostakovsky, F. P. Sidelkovskaya, and E. S. Shapiro	997	1085
Macromolecular Compounds. Communication 83. Synthesis of Polyalkylenecycloalkyls. V. V. Korshak and G. S. Kolesnikov	1001	1090
Macromolecular Compounds. Communication 84. Polycondensation of 1,2-Dichloroethane with Toluene. G. S. Kolesnikov, V. V. Korshak, and T. A. Soboleva . . .	1007	1095
Macromolecular Compounds. Communication 85. Polycondensation of 1,2-Dichloroethane with o-Dichlorobenzene. G. S. Kolesnikov, and V. V. Korshak	1011	1100
Macromolecular Compounds. Communication 86. Determination of the Molecular Weights of Polyamides from the Viscosities of Their Solutions in Cresol and in Methanol. V. V. Korshak and S. A. Pavlova	1017	1107
Polycondensation of Glycine Ethyl Ester. V. V. Korshak, K. T. Poroshin, and T. D. Kozarenko	1023	1112

Page Russ. Page

Brief Communications

Isomerization of Ethylcyclopropane on Silica Gel Under the Conditions of Chromatographic Adsorption Analysis. B. A. Kazansky, V. T. Aleksanyan, M. Yu. Lukina, A. L Malyshev, and Kh. E. Sterin 1029 1118

Dependence of the Kinetics of the Decomposition of Cyclohexene on the Structure of the Catalyst. E. K. Mankash and V. V. Shchekin 1031 1119

Synthesis and Properties of (1-Cyano-1-Methylethoxy)Silanes. A. D. Petrov, V. F. Mironov, and V. M. Vdovin 1035 1122

Organoboron Compounds. Communication 4. Synthesis of Dialkylborinic Esters With the Aid of Lithium Reagents. B. M. Mikhailov and T. A. Shchegoleva 1039 1124

Current Events

General Meeting of the Division of Chemical Sciences of the U. S. S. R. Academy of Sciences on the Peaceful Uses of Atomic Energy 1041 1126

AUTHOR INDEX

1955

Agronomov, A. E., see Shuikin, N. I.
Aleksanyan, V. T., see Kazansky, B. A.
Alimov, P. I., see Arbuzov, B. A.
Alimov, P. I. and I. V. Cheplanova. Synthesis of alkyl bis [1-(diethoxyphosphinyl) alkyl] phosphites, 929.
Alimov, P. I. and O. N. Fedorova. Some derivatives of 1-hydroxyalkylphosphinic acids, 761.
Andreev, D. N., B. N. Dolgov, and E. V. Kukharskaya. Synthesis of organosilicon esters of propionic and isobutyric acids, and their properties, 465.
Andreev, V. M., see Nazarov, I. N.
Andrianov, K. A., N. N. Sokolov, E. N. Khrustaleva, and L. N. Yukina. Reactions of epichlorohydrin and of glycidol with organochlorosilanes, 469. (Epichlorohydrin)
Anisimov, K. N., N. E. Kolobova, and A. N. Nesmeyanov. Derivatives of unsaturated phosphonic acids. Communication 5. Esters of 2-ethoxy-, 2-propoxy-, 2-butoxy-, and 2-hexyloxy-vinylphosphonic acids, 213.
Anisimov, K. N., N. E. Kolobova and A. N. Nesmeyanov. Derivatives of unsaturated phosphonic acids. Communication 6. Diesters of 2-isopropoxy-, 2-isobutoxy-, and 2-isopentyloxyvinylphosphonic acids, 377.
Anisimov, K. N., N. E. Kolobova, and A. N. Nesmeyanov. Derivatives of unsaturated phosphonic acids. Communication 7. Diesters of 2-phenoxyvinylphosphonic acid, 383.
Anisimov, K. N., N. E. Kolobova and A. N. Nesmeyanov. Derivatives of unsaturated phosphonic acids. Communication 8. Bisdialkylamides of 2-alkoxy- and 2-phenoxyvinylphosphinic acids, 591.
Anisimov, K. N., N. E. Kolobova and A. N. Nesmeyanov. Derivatives of unsaturated phosphonic acids. Communication 9. Diesters of 2-alkoxy- and 2-phenoxyvinylphosphonothionic acids, 595.
Anisimov, K. N., N. E. Kolobova and A. N. Nesmeyanov. Derivatives of unsaturated phosphonic acids. Communication 10. Diesters of 2-alkoxy- and 2-phenoxyvinylphosphonodithiolic and of 2-alkoxy- and 2-phenoxy-vinyl phosphonotrithioic acids, 741.
Anisimov, K. N., N. E. Kolobova and A. N. Nesmeyanov. Derivatives of unsaturated phosphonic acids. Communication 11. Diesters of 2-(2-alkoxyethoxy)vinylphosphonic acids, 745.
Anisimov, K. N., N. E. Kolobova and A. N. Nesmeyanov. Derivatives of unsaturated phosphonic acids. Communication 12. Bisdialkylamides of 2-(2-alkoxythoxy)vinylphosphonic acids, 751.
Anisimov. K. N., N. E. Kolobova, and A. N. Nesmeyanov. Derivatives of unsaturated phosphonic acids. Communication 13. Diesters of 2-(2-alkoxyethoxy) vinylphosphonomono-, di- and tri-thioic acids. 911.
Anisimov, K. N., and A. N. Nesmeyanov. Derivatives of unsaturated phosphonic acids. Communication 14. Diesters of styrylphosphonic acid, 915.
Anisimov, K. N., and A. N. Nesmeyanov. Derivatives of unsaturated phosphonic acids. Communication 15. Diesters of β-chlorostyrylphosphonic acid and phenylethynylphosphonic acids, 919.
Antonova, I. N., V. A. Kuzmin, R. I. Moskina, A. B. Nalbandyan, M. B. Neiman and G. I. Feklisov. Study, with the aid of labeled atoms, of the reaction mechanism of the oxidation of methane. Mechanism of formation of carbon monoxide, 711.
Arbuzov, B. A., and P. I. Alimov. The products of the action of sodium diethylphosphorothionate on alkyl phosphorodichloridites, 221.
Arbuzov, B. A., K. V. Nikonorov and G. M. Vinokurova. Some esters of phosphorodithioic acid as insecticides, 597.
Arbuzov, B. A., and N. I. Rizpolozhensky. Esters of ethylphosphonous acid, and some of their reactions. Communication 5. Synthesis of esters of dialkylphosphinic acids, 225.
Arbuzov, B. A., N. I. Rizpolozhensky, and M. A. Zvereva. Esters of ethylphosphonous acid, and some of their reactions. Communication 6. Triethylphosphoamidous esters, 935.
Arbuzov, B. A., and O. D. Samoilova. Action of some alkoxy compounds on trialkoxy- and dialkoxychloro-stibines, 385.
Arbuzov, B. A. and O. D. Samoilova. Action of halogens on esters of antimonous acid, 601.

Arbuzov, B. A., and V. S. Vinogradova. Parachors of trialkylmethylsilanes, 1945.

Arbuzov, B. A., and V. M. Zoroastrova. Synthesis of phosphonic esters containing heterocyclic radicals. Communication 5. Phosphonic esters containing a hydrocoumarin radical, 605.

Aronovich, P. M., see Mikhailov, B. M.

Atavin, A. S., see Shostakovsky, M. F.

Avramenko, L. I. and R. V. Kolesnikova. Experimental determination of the sequence of successive elementary reactions of atoms and radicals, 345.

Balandin, A. A. Present state of the catalysis problem and the theoretical basis of the search for catalysis, 557.

Balandin, A. A., O. K. Bogdanova, and A. P. Shcheglova. Free energy change in the adsorptional displacement of butene by water from a catalyst surface, 643.

Baranetskaya, N. K., see Setkina, V. N.

Batsanov, S. S., see Boky, G. B.

Batuev, M. L., see Meshcheryakov, A. P.

Batuev, M. I., see Shostakovsky, M. F.

Berdnikova, N. G. see Shuikin, N. I.

Bering, B. P., and K. A. Ioileva. Adsorption of vapor at a mercury surface. Communication 1, 7.

Bering, B. P., and K. A. Ioileva. Adsorption of vapor at a mercury surface. Communication 2, 193.

Blokhina, A. N., see Mikhailov, B. M.

Bogdanova, O. K., see Balandin, A. A.

Boikova, A. I., see Toropov, N. A.

Boky, G. B., and S. S. Batsanov. Crystal-optical method for determining the structures of complex compounds, 173.

Bondar, I. A., see Toropov, N. A.

Borunova, N. V., see Rubinshtein, A. M.

Brainina, E. M., see Nesmeyanov, A. N.

Chekulaeva, I. A., see Shostakovsky, M. F.

Cheltsova, M. A., E. A. Chernyshev, and A. D. Petrov. Behavior of 3-, 4-, and 5-alkenyl halides in condensation reactions with alkyl halides in condensation reactions with alkyl halides in presence of magnesium, 459.

Cheplanova, I. V., see Alimov, P. I.

Chernyshev, E. A., see Cheltsova, M. A.

Dobrynina, T. A., see Makarov, S. Z.

Dobrynina, T. A., see Rode, T. V.

Dobrynina, T. P., see Shuikin, N. I.

Dolgov, B. N., see Andreev, D. N.

Dombrovsky, Ya. V., see Nesmeyanov, A. N.

Dubinin, M. M., and E. D. Zaverina. Surface and sorption properties of active carbons. Communication 1. Sorption isotherms for benzene and water vapor, 531.

Dubrovo, S. K., and Yu. A. Shmidt. Reaction of vitreous sodium silicates and aluminosilicates with aqueous solutions. Communication 6. Reaction of vitreous sodium silicates and aluminosilicates with caustic alkali solutions, 359.

Dubrovo, S. K., and Yu. A. Shmidt. Reaction of vitreous sodium silicates and aluminosilicates with aqueous solutions. Communication 7. Reaction of vitreous Sodium silicates and aluninosilicates with salt solutions, 539.

Egorov, Yu. P., see Petrov, A. D.

Egorov, Yu. P., see Shuikin, N. I.

Emelyanova, L. I., see Nesmeyanov, A. N.

Fedorova, L. S., see Kolesnikov, G. S.

Fedorova, O. N., see Alimov, P. I.

Feklisov, G. I., see Antonova, I. N.

Feofanova, L. M., see Shuikin, N. I.

Filipovich, V. N., see Porai-Koshits, E. A.

Florinsky, F. S., see Koton, M. M.

Fodor, G., J. Toth, E. Kovacs, and J. Kiss. Synthesis of chloramphenicol, 391.

Fokin, A. V., see Knunyants, I. L.

Fokina, E. A., see Zhabrova, G. M.

Freidlin, L. Kh., see Rubinshtein, A. M.

Freidlina, R. Kh., V. N. Kost and A. N. Nesmeyanov. Chlorination and dehydrochlorination of polychloro compounds containing reactive groups, 207.

Freidlina, R. Kh., see Nesmeyanov, A. N.

Frunze, T. M., see Korshak, V. V.

Galakhov, F. Ya., see Toropov, N. A.

Galpern, G. D., see Karaulova, E. N.

Gambaryan, N. P., see Knunyants, I. L.

Gladyshevskaya, V. A., see Shostakovsky, M. F.

Golder, G. A., see Rode, T. V.

Goldfarb, Ya. L., and M. L. Kirmalova. Synthesis and reactions of some 2,2'- methylenedithiophene derivatives, 509.

Golova, O. P. and N. S. Mayat. Comparative study of the oxidation reactions of pectic substances, of cellulose, and of the structural units of these substances. Communication 2. Oxidative degradation of sodium polygalacturonate by means of molecular oxygen, sodium metaperiodate, and hydrogen peroxide, 815.

Golova, O. P. and N. S. Mayat. Comparative study of the oxidation reactions of pectic substances, of cellulose, and of the structural units of these substances. Communication 3. Comparative study of the reactivities of the structural units of cellulose and pectic substances in oxidation reactions with sodium metaperiodate and hydrogen peroxide, 991.

Gorbunov, N. S. Physicochemical basis of the formation of diffusional surface layers on iron and its alloys, 715.

Gostunskaya, I. V., G. V. Loza, and B. A. Kazansky. Catalytic hydrogenation of doubly unsaturated compounds having a conjugated system of double bonds. Communication 3. Hydrogenation of 2,3-dimethyl-1,3-butadiene in presence of platinum, nickel, and palladium, 779.

Grigoryeva, N. K., see Makarov, S. Z.

Grinberg. A. A., and G. A. Shagisultanova. Kinetics of bromine exchange in complex platinum bromides, 895.

Ignatenok, P. G., see Knunyants, I. L.

Ioffe, E. M. Interphase partition in systems containing anomalous mixed crystals. Communication 4. The systems NH_4-$CuCl_2$-H_2O and NH_4Cl-$CrCl_3$-H_2O, 525.

Ioileva, K. A., see Bering, B. P.

Kabachnik, M. I. Theory of tautomeric equilibrium in solution. Effect of solvation on the equilibrium between the keto and isomeric cis and trans enol forms, 85.

Kabachnik, M. I., see Medved, T. Ya.

Karaulova, E. N., and G. D. Galpern. Reactions of 2-bromoethyl phenyl ether in presence of zinc chloride and a mixture of zinc and aluminum chlorides. 865.

Kazansky, B. A., V. T. Aleksanyan, M. Yu. Lukina, A. I. Malyshev, and Kh. E. Sterin. Isomerization of ethylcyclopropane on silica gel under the conditions of chromatographic adsorption analysis, 1029.

Kazansky, B. A., see Gostunskaya, I. V.

Kharkharov, A. A. Absorption spectra and molecular structure. Communication 3. Modern electronic theory, and the color of arylhydrazones of 9-acridinecarboxaldehyde, 293.

Kharkharov, A. A. Absorption spectra and molecular structure. Communication 4. Effect of the character of the substituent on color in derivatives of 9-acridinecarboxaldehyde phenylhydrazone hydrochloride 795.

Kharkharov, A. A. Absorption spectra and molecular structure. Communication 5. Spectroscopic investigations of solutions of chlorine-substituted phenylhydrazones of 9-acridinecarboxaldehyde hydrochloride in alcoholic hydrogen chloride, 983.

Khomutov, A. M., see Shostakovsky, M. F.

Khrustaleva, E. N., see Andrianov, K. A.

Khurgin, Yu. I., see Poroshin, K. T.

Kildisheva, O. V., see Knunyants, I. L.

Kildisheva, O. V., M. G. Linkova, and I. L. Knunyants. Reactions of mercapto amino acids. Communication 6. 2-Acylamino-3-haloacrylic acids and their derivatives, 251.

Kildisheva, O. V., see Knunyants, I. L.

Kildisheva, O. V., see Linkova, M. G.

Kildisheva, O. V., M. G. Linkova, and I. L. Knunyants. Reactions of mercapto amino acids. Communication 5. N-Acyl-3-halo-2-hydroxyalanines and their derivatives, 241.

Kildisheva, O. V., M. G. Linkova, and I. L. Knunyants. Reactions of mercapto amino acids. Communication 7. Reactions of N-acyl-2,3-dihaloalanines. (Acyloxy) pyruvic acids, 401.

Kildisheva, O. V., L. P. Rasteikene, and I. L. Knunyants. Reactions of mercapto amino acids. Communication 4. N-Acyl-2,3-dihaloalanines, 231.

Kirmalova, M. L., see Goldfarb, Ya. L.

Kiseleva, T. M., see Koton, M. M.

Kiss, J., see Fodor, G.

Klokman, V. R., V. K. Zinovyeva and I. A. Tseveleva. Determination of the crystallizational coefficient for the distribution of a thorium B (radioactive lead) salt between a salt melt and crystals of an isomorphous salt, 721.

Knunyants, I. L., and A. V. Fokin. Addition reactions of perfluoroolefins. Communication 3. Addition of sulfur chlorides, 627.

Knunyants, I. L., and N. P. Gambaryan. New method of preparing β-lactams, 951.

Knunyants, I. L., see Kildisheva, O. V.

Knunyants, I. L., O. V. Kildisheva, and M. G. Linkova. Reactions of mercapto amino acids. Communication 3. Acylation and alkylation of 3,3-dimethylcysteine, 61.

Knunyants, I. L., O. V. Kildisheva, and E. Ya. Pervova. Reactions of mercapto amino acids. Communication 9. Synthesis of α-acylamino-β-thiolactones, 613.

Knunyants, I. L., O. V. Kildisheva and E. Ya. Pervova. Reactions of mercapto amino acids. Communication 10. New method for the synthesis of polypeptides, 619.

Knunyants, I. L., see Linkova, M. G.

Knunyants, I. L., and M. G. Linkova. Reactions of mercapto amino acids. Communication 2. Acylation and alkylation of 3,3-dimethylcysteine, 53.

Knunyants, I. L., M. G. Linkova, and P. G. Ignatenok. Reactions of mercapto amino acids. Communication 1. 3,3-dimethylisocysteine and its derivatives, 47.

Knunyants, I. L., and V. Ya. Pilskaya. New method for the preparation of primary and secondary organoarsenic compounds, 417.

Knunyants, I. L., and V. V. Shokina. Reactions of mercapto amino acids. Communication 8. Alkylation and acylation of cysteine and 3,3,-dimethylcysteine by derivatives of N-acyl-3-haloalanines, 409.

Knunyants, I. L. and E. G. Vykhovskaya. Addition reactions of perfluoroolefins. Communication 4. Reaction of vinylidene fluoride with sulfur chlorides and with alkanesulfenyl chlorides, 769.

Kochesnkov, K. A., and E. M. Panov. Compounds of the classes Ar_2PbX_2 and $ArPbX_3$ in the p-tolyl series, 639.

Kochesnkov, K. A., and E. M. Panov. Dearylation of Ar_2PbX_2 as a method of synthesizing a new class of compounds $ArPbX_3$, 633.

Kochetkov, N. K., L. I. Kudryashov and A. N. Nesmeyanov. Reaction of alkyl 2-chlorovinyl ketones with ethyl acetoacetate, 729.

Kochetkov, N. K., see Nesmeyanov, A. N.

Kochkin, D. A., see Shostakovsky, M. F.

Kolesnikov, G. S., and V. V. Korshak. Macromolecular compounds. Communication 85. Polycondensation of 1,2-dichloroethane with o-dichlorobenzene, 1011.

Kolesnikov, G. S., see Korshak, V. V.

Kolesnikov, G. S., V. V. Korshak, and L. S. Fedorova. Macromolecular compounds. Communication 71. Polycondensation of 1,2-chloroethane with chlorobenzene in presence of aluminum chloride, 321.

Kolesnikov, G. S., V. V. Korshak and T. V. Smirnova. Macromolecular compounds. Communication 70. Peculiar features of chain growth during polycondensation in presence of a catalyst, 151.

Kolesnikov, G. S., V. V. Korshak, and T. A. Soboleva. Macromolecular compounds. Communication 84. Polycondensation of 1,2-dichloroethane with toluene, 1007.

Kolesnikova, R. V., see Avramenko, L. I.

Kolobova, N. E., see Anisimov, K. N.

Kononova, T. A., see Ushakov, S. N.

Korshak, V. V., and T. M. Frunze. Macromolecular compounds. Communication 69. Dependence of the properties of polyamides on the extent of intermolecular hydrogen bonding, 143.

Korshak, V. V., and T. M. Frunze. Macromolecular compounds. Communication 73. Some two-component mixed polyamides, 333.

Korshak, V. V., and T. M. Frunze. Macromolecular compounds. Communication 74. Effect of aromatic components on the properties of mixed polyamides, 487.

Korshak, V. V., and T. M. Frunze. Macromolecular compounds. Communication 75. Dependence of the properties of polyamides on the extent of intermolecular hydrogen bonding, 493.

Korshak, V. V., and T. M. Frunze. Macromolecular compounds. Communication 76. Role of exchange reactions in polyamide formation, 499.

Korshak, V. V., and T. M. Frunze. Macromolecular compounds. Communication 77. Dependence of the properties of aliphatic polyamides having "even" repeating units on the structure of the repeating unit, 673.

Korshak, V. V., and T. M. Frunze. Macromolecular compounds, Communication 78. Dependence of the properties of aliphatic polyamides having "odd" repeating units on the structure of the repeating unit, 679.

Korshak, V. V. and T. M. Frunze. Macromolecular compounds. Communication 81. Mixed polyamides containing glutaric or pimelic acid residues, 849.

Korshak, V. V., see Kolesnikov, G. S.

Korshak, V. V., and G. S. Kolesnikov. Macromolecular compounds. Communication 83. Synthesis of polyalkylenecycloalkyls, 1001.

Korshak, V. V., G. S. Kolesnikov and T. A. Soboleva. Macromolecular compounds. Communication 72. Formation of a three-dimensional polymer by reaction of poly [ethylenephenyl] with dihaloalkanes, 327.

Korshak, V. V., and N. G. Matveeva. Macromolecular compounds. Communication 82. 2,4,5-Triisopropyl-α-methylstyrene, 855.

Korshak, V. V., and S. A. Pavlova. Macromolecular compounds. Communication 86. Determination of the molecular weights of polyamides from the viscosities of their solutions in cresol and methanol, 1017.

Korshak, V. V., K. T. Poroshin, and T. D. Kozarenko. Polycondensation of glycine ethyl ester, 1023.

Korshak, V. V., and S. V. Vinogradova. Macromolecular compounds. Communication 79. Products of the polycondensation of dialdehydes and diketones with diamines and glycols, 841.

Korshak, V. V. and S. V. Vinogradova. Macromolecular compounds, Communication 80. A case of migrational copolymerization, 845.

Kost, T. A., see Nesmeyanov, A. N.

Kost, V. N., see Freidlina, R. Kh.

Koton, M. M., T. M. Kiseleva and F. S. Florinsky. Synthesis of 2,2'-azobis [2-methylpropionitrile] labeled with radioactive carbon (C^{14}), 555.

Koton, M. M., and V. F. Martynova. Reactions of symmetrical aromatic mercury compounds with phenols, 975.

Kovacs, E., see Fodor, G.

Kozarenko, T. D., see Korshak, V. V.

Kozarenko, T. D., see Poroshin, K. T.

Krentsel, B. A., see Tolchinsky, I. M.

Kucherov, V. F., see Nazarov, I. N.

Kudryashov, L. I., see Kochetkov, N. K.

Kugatova, G. P., see Nazarov, I. N.

Kukharskaya, E. V., see Andreev, D. N.

Kursanov, D. N., see Setkina, V. N.

Kuzmin, V. A., see Antanova, I. N.

Lebedev, B. A., see Makarov, S. Z.

Leonov, A. I. Role of dissociational activation in the sintering of oxides of elements of variable valency, 725.

Levin, D. I., see Porai-Koshits, E. A.

Levin, D. I., see Zhdanov, S. P.

Levin, D. I., S. P. Zhdanov, and E. A. Porai-Koshits. Structure of sodium borosilicate glasses in its relation to the phenomenon of opalescence Communication 1. Investigation of the opalescence of glasses, 27.

Liberman, G. S., see Nesmeyanov, A. N.

Linkova, M. G., see Kildisheva, O. V.

Linkova, M. G., O. V. Kildisheva, and I. L. Knunyants. β-Thiolactones, 507.

Linkova, M. G., see Knunyants, I. L.

Loza, G. V., see Gostunskaya, I. V.

Lukina, M. Yu., see Kazansky, B. A,

Mairanovsky, S. G., and M. B. Neiman. Equation for the diffusion current at a dropping electrode taking into account the screening of part of the electrode surface, 373.

Makarov, S. Z. and T. A. Dobrynina. Systems containing hydrogen peroxide at high concentration. Communication 9. The ternary system $LiOH\text{-}H_2O_2\text{-}H_2O$, 365.

Makarov, S. Z., and N. K. Grigoryeva. Systems containing hydrogen peroxide at high concentration. Communication 7. 0° isotherm of the ternary system $NaOH\text{-}H_2O_2\text{-}H_2O$, 15.

Makarov, S. Z., and N. K. Grigoryeva. Systems containing hydrogen peroxide at high concentration. Communication 8. Thermal characteristics and stabilities of solid phases of the system $NaOH\text{-}H_2O_2\text{-}H_2O$, 187.

Makarov, S. Z., and B. A. Lebedev. Systems containing hydrogen peroxide at high concentration. Communication 10. Thermal stability of urea perhydrate, 705.

Malyshev, A. I., see Kazansky, B. A.

Mankash, E. K., and V. V. Shchekin. Dependence of the kinetics of the decomposition of cyclohexene on the structure of the catalyst, 1031.

Martynova, V. F., see Koton, M. M.

Materikova, R. B., see Nesmeyanov, A. N.

Matveeva, N. G. see Korshak, V. V.

Matveeva, A. D., see Meshcheryakov, A. P.

Matveeva, A. D., see Shostakovsky, M. F.

Mayat, N. S., see Golova, O. P.

Medelyanovskaya, M. A., see Shostakovsky, M. F.

Medved, T. Ya., and M. I. Kabachnik. Acylation of aminoalkylphosphonic and aminoalkylphosphonothioic acid, 957.

Medved, T. Ya. and M. I. Kabachnik. Methylation of 1-aminoalkylphosphonic acids and their esters, 961.

Melekhin, V. M., see Petrov, A. D.

Meshcheryakov. A. P., M. I. Batuev, and A. D. Mateeva. Synthesis of tert-butyl hydroperoxide and tert-butyl peroxide and their optical investigation in relation to the problem of the structure of hydrogen peroxide, 661.

Meshcheryakov, A. P., and L. V. Petrova. Reactions of 3,3,4-trimethyl-2-pentanol, 969.

Mikhailov, B. M., and P. M. Aronovich. Preparation of p-terphenyl, 857.

Mikhailov, B. M., and P. M. Aronovich. Organoboron compounds. Communication 3. Preparation of the isobutyl esters of phenylpropyl- and butylphenyl borinic acids, 859.

Mikhailov, B. M. and A. N. Blokhina. Complex nature of dimetal compounds of phenazine, 775.

Mikhailov, B. M., and A. N. Blokhina. Photodehydrocondensation of anisole homologs. Photosynthesis of synestrol, 289.

Mikhailov, B. M., and T. A. Shchegoleva. Organoboron compounds. Communication 4. Synthesis of dialkylborinic esters with the aid of lithium reagents, 1039.

Minachev, Kh. M., see Shuikin, N. I.

Mironov, V. F., A. D. Petrov, and N. A. Pogonkina. Cyanoethylation of organosilicon amines, 685.

Mironov, V. D., and N. A. Pogonkina. Synthesis of 3- and 4-alkenyltrialkylsilanes, 161.

Moshkina, R. I., see Antanova, I. N.

Murin, A. N., B. K. Preobrazhensky and N. E. Titov. Radiochemical investigation of spallation and fission reaction products resulting from the bombardment of bismuth with 660-Mev protons, 517.

Nalbandyan, A. B., see Antanova, I. N.

Nazarov, I. N., and V. F. Kucherov. Stereochemistry of cyclic compounds. Communication 7. Geometric isomerism of 4-methyl-1,2-cyclohexanedicarboxylic acids, 265.

Nazarov, I. N., V. F. Kucherov, and V. M. Andreev. Stereochemistry of cyclic compounds. Communication 4. Condensation of 1-vinylcyclohexene with citraconic anhydride, 67.

Nazarov, I. N., V. F. Kucherov, and V. M. Andreev. Stereochemistry of cyclic compounds. Communication 5. Condensation of 1-vinylcyclohexene with dimethyl mesaconate, 77.

Nazarov, I. N., V. F. Kucherov, and V. M. Andreev. Stereochemistry of cyclic compounds. Communication 6. Lactonization of cis- and trans-1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acids, 257.

Nazarov, I. N., V. F. Kucherov, and G. P. Kugatova. Stereochemistry of cyclic compounds. Communication 8. Condensation of cis-1,2,4a, 5,8,8a-hexahydro-4a,7-dimethyl-4-vinylnaphthalene with citraconic anhydride, 429.

Nazarov, I. N., and G. P. Kugatova. Synthesis of steroid compounds and related substances. Communication 29. Condensation of isoprene with 2-methyl-2-cyclohexen-1-one Synthesis of cis-1,2,4a,5,8,8a-hexahydro-4a,7-dimethyl-4-vinylnaphthalene, 423.

Nefedov, A. M., see Petrov, A. D.

Neiman, M. B., see Antonova, I. N.

Neiman, M. B., see Mairanovsky, S. G.

Nekrasova, V. A., and N. I. Shuikin. Chlorination of dodecane, 867.

Nesmeyanov, A. N., see Anisimov, K. N.

Nesmeyanov, A. N., E. M. Brainina and R. Kh. Freidlina. Synthesis of alkoxybromotitaniums and alkoxychloropolytitanoxanes, 755.

Nesmeyanov, A. N., see Freidlina, R. Kh.

Nesmeyanov, A. N. R. Kh. Freidlina, and N. A. Semenov. Condensation of 3,3,3-trichloropropene with aromatic compounds, 905.

Nesmeyanov, A. N., see Kochetkov, N. K.

Nesmeyanov, A. N., N. K. Kochetkov, and Ya. V. Dombrovsky. 2-aminovinyl ketones. Communication 2. Synthesis of alkyl 2-aminovinyl ketones, 157.

Nesmeyanov, A. N., N. K. Kochetkov, M. I. Rybinskaya and E. V. Uglova. Some reactions of alkyl 2-phenoxyvinyl ketones, 579.

Nesmeyanov, A. N., M. I. Rybinskaya and N. K. Kochetkov. Reaction of 2-chlorovinyl ketones with anthracene, 735.

Nesmeyanov, A. N., and V. A. Sazonova. Synthesis of sodium tetraphenylboron, 167.

Nesmeyanov, A. N. V. A. Sazonova, G. S. Liberman and L. I. Emelyanova. Reactions

of organomagnesium compounds with potassium and triethyloxonium fluoborates, 41.
Nesmeyanov, A. N., V. A. Sazonova, and R. B. Materikova. Reactions of fenchone with organomagnesium and organolithium compounds, 901.
Nesmeyanov, A. N., and L. I. Zakharkin. ω-chloro carboxylic acids, and some of their reactions, 199.
Nesmeyanov, A. N., L. I. Zakharkin and R. Kh. Freidlina. Preparation of carboxylic acids of structure $CCl_3(CH_2)nCOOH$ and $CCl_2=$ $=CH(CH_2)nCOOH$, and their dissociation constants, 35.
Nesmeyanov, A. N., L. I. Zakharkin and T. A. Kost. Synthesis of dodecanedioic and hexadecanedioic acids, 585.
Nikishin, G. I., see Petrov, A. D.
Nikonorov, K. V., see Arbuzov, B. A.

Obreimov, I. V. and T. N. Shkurina. Identification of hydrocarbons with aid of dispersion curves, 805.

Panov, E. M., see Kocheshkov, K. A.
Pavlova, S. A., see Korshak, V. V.
Pervova, E. Ya., see Knunyants, I. L.
Petrov, A. D. Synthesis of branched aliphatic hydrocarbons via 2-alkenyl halides, 571.
Petrov, A. D., see Cheltsova, M. A.
Petrov, A. D., Melekhin, V. M., and A. M. Nefedov. Reaction of 2-methylallylmagnesium chloride with esters of palmitic and 2-ethylhexanoic acids, 339.
Petrov, A. D., see Mironov, V. F.
Petrov, A. D., V. F. Mironov, and V. M. Vdovin. Synthesis and properties of (1-cyano-1-methylethoxy) silanes, 1035.
Petrov, A. D., G. I. Nikishin, N. P. Smetankina, and Yu. P. Egorov. Synthesis of 1,1-dichlorosilacyclopent-3-ene, 861.
Petrov, A. D., S. I. Sadykhzade, and V. M. Vdovin. Reaction of 3-buten-1-ynylmagnesium bromide with halotriphenylsilanes, 159.
Petrova, L. V., see Meshcheryakov, A. P.
Pilskaya, V. Ya., see Knunyants, I. L.
Pogonikina, N. A., see Mironov, V. F.
Popov, M. A., and N. I. Shuikin. Catalytic amination of alcohols, 275.
Porai-Koshits, E. A., and V. N. Filipovich. Babinet's principle, and the low-angle scattering of x-rays by porous glasses, 19.
Porai-Koshits, E. A., see Levin, D. I.
Porai-Koshits, E. A., see Zhdanov, S. P.
Porai-Koshits, E. A., S. P. Zhdanov, and D. I. Levin. Structure of sodium borosilicate glasses in its relation to the phenomenon of opalescence. Communication 3. Comparison of the results of investigations of sodium borosilicate glasses and on porous products obtained from them by leaching, 353.
Poroshin, K. T., see Korshak, V. V.
Poroshin, K. T., T. D. Kozarenko, and Yu. I. Khurgin. Quantitative determination of 2,5-piperazinediones in the products of the polycondensation of esters of α-amino acids, 693.
Preobrazhensky, B. K., see Murin, A. N.
Pribytkova, N. A., see Rubinshtein, A. M.
Prilezhaeva, E. N., see Shostakovsky, M. F.

Rasteikene, L. P., see Kildisheva, O. V.
Rizpolozhensky, N. I., see Arbuzov, B. A.
Rode, T. V., T. A. Dobrynina and G. A. Golder. Physicochemical study of lithium peroxide, 545.
Rog, V. M., see Shostakovsky, M. F.
Rubinshtein, A. M., L. Kh., Freidlina and N. V. Borunova. Catalytic inertness of amorphous nickel in the hydrogenation of benzene and the dehydrogenation of cyclohexane, 683.
Rubinshtein, A. M., and N. A. Pribytkova. Effect of the structural factor on the catalytic decomposition of alcohols varying in molecular weight, 689.
Rybinskaya, M. I., see Nesmeyanov, A. N.

Sadykhazade, S. I., see Petrov, A. D.
Samoilov. O. Ya. Relation between the mobilities of ions in solution and their self-diffusion coefficients, 513.
Samoilova, O. D., see Arbuzov, B. A.
Sazonova, V. A., see Nesmeyanov, A. N.
Shmidt, Yu. A., see Dubrovo, S. K.
Semenov, N. A., see Nesmeyanov, A. N.
Setkina, V. N., N. K. Baranetskaya, and D. N. Kursanov. Exchange and cleavage reactions of quaternary ammonium salts. Communication 2. Reaction of quaternary ammonium salts of the type $[R-O-CH_2-N-]X$ with secondary and tertiary alcohols, 667.
Shagisultanova, G. A., see Grinberg, A. A.

Shapiro, E. S., see Shostakovsky, M. F.

Shcheglova, A. P., see Balandin, A. A.

Shchegoleva. T. A., see Mikhailov, B. M.

Shchekin, V. V., see Mankash, E. K.

Shkurina, T. N., see Obreimov, I. V.

Shokina, V. V., see Knunyants, I. L.

Shostakovsky, M. F., A. S. Atavin, and V. V. Zhebrovsky. Reactions between vinyl compounds and multifunctional compounds. Communication 6. Reaction of vinyl ethers with pentaerythritol, 477.

Shostakovsky, M. F., M. I. Batuev, I. A. Chekulaeva, and A. D. Matveeva. Optical investigation of some vinyl ethers of ethanolamines, 481.

Shostakovsky, M. F., and I. A. Chekulaeva. Synthesis and reactions of vinyl ethers of ethanolamines. Communication 6. Vinyl ether of 2-anilinoethanol, 127.

Shostakovsky, M. F., and I. A. Chekulaeva. Synthesis and reactions of vinyl ethers of ethanolamines. Communication 7. Vinyl ether of 2-diphenylaminoethanol, 829.

Shostakovsky, M. D., and V. A. Gladyshevskaya. Polymerization of vinyl compounds. Communication 1. Stepwise shythesis of poly (butylvinyl ether), 121.

Shostakovsky, M. F. and V. A. Gladyshevskaya. Polymerization of vinyl compounds. Communication 2. Stepwise synthesis of poly (ethyl vinyl ether), 309.

Shostakovsky, M. F., and A. M. Khomutov. Reactions of unsaturated and macromolecular compounds. Communication 4. Copolymerization of some vinly compounds with 2-vinyloxyethanol, 109.

Shostakovsky, M. F., and A. M. Khomutov. Reactions of unsaturated and macromolecular compounds. Communication 5. Copolymerization of methyl acrylate with vinyl ethers, 115.

Shostakovsky, M. F., D. A. Kochkin, and V. M. Rog. Synthesis and reactions of oxygen-containing organosilicon compounds. Communication 21. Reactions of diethyl- and diphenyl-silanediols with vinyl ethers, 871.

Shostakovsky, M. F., E. N. Prilezhaeva, and E. S. Shapiro. Synthesis of sulfur compounds by the aid of vinyl ethers and acetylene. Communication 12. The most effective catalysts for the addition of hydrogen sulfide to vinyl ethers in the direction contrary to Markovnikov's rule, 653.

Shostakovsky, M. F., E. N. Prilezhaeva, and N. I. Uvarova. Synthesis of sulfur compounds by the aid of vinyl ether and acetylene. Communication II. Ion-catalyzed reactions of ethyl vinyl sulfide, 135.

Shostakovsky, M. F., E. N. Prilezhaeva, and N. I. Uvarova. Synthesis of sulfur compounds by the aid of vinyl ethers and acetylene. Communication 13. General methods for the synthesis of vinyl sulfides, 821.

Shostakovsky, M. F., F. P. Sidelkovskaya, and A. M. Khomutov. Reactions of unsaturated and macromolecular compounds, Communication 6. Copolymerization of vinylcaprolactam with methyl methacrylate in presence of benzoyl peroxide and of 2,2' -azobis [2-methylpropionitrile], 835.

Shostakovsky, M. F., F. P. Sidelovskaya, and E. S. Shapiro. Polymerization of isopropyl vinyl and cyclohexyl vinyl ethers in presence of 2,2' -azobis [2-methylpropionitrile], 997.

Shostakovsky, M. F., V. V. Zhebrovsky, and M. A. Medelyanovskaya. Reactions between vinyl compounds and multifunctional compounds. Communication 4. Reaction of alkyl vinyl ethers with glycerol and with glycerol-1,2- and 1,3-cyclic acetals, 313.

Shostakovsky, M. F. V. V. Zhebrovsky, and M. A. Medelyanovskaya. Reactions between vinyl compounds and multifunctional compounds. Communication 5. Reaction of glycerol trivinyl ether with monohydric alcohols, 317. (Table of contents has ester)

Shuikin, N. I., and N. G. Berdnikova. High-temperature contact-catalysis reactions of benzene and its closest homologs in presence of hydrogen at high pressure, 95.

Shuikin, N. I., T. P. Dobrynina, E. A. Timofeeva, and Yu. P. Egorov. Catalytic dehydrogenation of isopentane, 869.

Shuikin, N. I., Kh. M. Minachev, L. M. Feofanova, E. G. Treshchova, T. P. Yudkina, and A. E. Agronomov. High - temperature reactions of methylcyclohexane in a continuous-flow system in presence of metals of the palladium group and of hydrogen at high pressure, 441.

Shuikin, N. I., see Nekrasova, V. A.

Shuikin, N. I., see Popov, M. A.

Shuikin, N. I., and E. A. Timofeeva. Reactions of individual hydrocarbons in contact with natural aluminosilicates. Communication 3. Reactions of cyclopentane ethylcyclopentane, ethylcyclohexane and ethylbenzene in

presence of Troshkov clay, 281.
Shuikin, N. I. and E. A. Timofeeva. Reforming of Tuimazin gasoline in contact with Troshkov Kaolin, 965.
Shuikin, N. I. E. A. Timofeeva, and V. M. Sladkikh. Contact-catalysis reactions of pentane in presence of chrome-alumina-magnesia catalyst, 503.
Shuikin, N. I., and V. A. Tulupov. Catalytic dehydrocyclization of piperylene, 785.
Sidelkovskaya, F. P., see Shostakovsky, M. F.
Sladkikh, V. M., see Shuikin, N. I.
Smetankina, N. P., see Petrov, A. D.
Smirnova, T. V., see Kolesnikov, G. S.
Soboleva, T. A., see Kolesnikov, G. S.
Soboleva, T. A., see Korshak, V. V.
Sokolov, N. N., see Andrianov, K. A.
Sterin, Kh. E., see Kazansky, B. A.

Timofeeva, E. A., see Shuikin, N. I.
Titov, N. E., see Murin, A. N.
Tolchinsky, I. M., B. A. Krentsel, and A. V. Topchiev. Destructive alkylation of benzene with pentane, 451.
Topchiev, A. V., see Tolchinsky, I. M.
Toropov, N. A., and A. I. Boikova. Solid solutions of calcium aluminoferrites, 887.
Toropov, N. A., F. Ya. Galakhov and I. A. Bondar. Field of solid solutions formed by celsian, dibarium trisilicate, and barium trisilicate, and barium disilicate (sanbornite), 1.
Toth, J., see Fodor, G.
Treshchova, E. G., see Shuikin, N. I.
Tseveleva, I. A., see Klokman, V. R.
Tulupov, V. A., see Shuikin, N. I.

Uglova, E. V., see Nesmeyanov, A. N.
Ushakov, S. N., and T. A. Konoova. Some physicochemical properties of esters of polyvinyl alcohol, 301.
Ushakov, S. N., and T. A. Kononova. Some physicomechanical properties of esters of polyvinyl alcohol, 301.
Ushakov, S. N., and T. A. Kononova. Synthesis of esters of polyvinyl alcohol, 103.
Uvarova, N. L., see Shostakovsky, M. F.
Vdovin, V. M., see Petrov, A. D.
Vinogradova, S. V., see Korshak, V. V.
Vinogradova, V. S., see Arbuzov, B. A.
Vinokurova, G. M., see Arbuzov, B. A.
Vykhovskaya, E. G., see Knunyants, I. L.

Yudkina, T. P., see Shuikin, N. I.
Yukina, L. N., see Andrianov, K. A.

Zakharkin, L. I. Action of sodium on coupounds containing a CCl_2=CH group, 923.
Zakharkin, L. I., see Nesmeyanov, A. N.
Zaverina, E. D., see Dubinin, M. M.
Zhabrova, G. M., and E. A. Fokina. Effect of the method of making modifying additions on the properties of oxide catalysts, 879.
Zhdanov, S. P., see Levin, D. I.
Zhdanov, S. P., see Porai-Koshits, E. A.
Zhdanov, S. P., E. A. Porai-Koshits and D. I. Levin. Structure of sodium borosilicate glasses in its relation to the phenomenon of opalescence. Communication 2. Investigation of the structure of porous glasses, 177.
Zhebrovsky, V. V., see Shostakovsky, M. F.
Zinovyeva, V. K., see Klokman, V. R.
Zoroastrova, V. M., see Arbuzov, B. A.
Zvereva, M. A., see Arbuzov, B. A.

SUBJECT INDEX

1955

Academy of Sciences of the USSR, Division of Chemical Sciences, current events, abstracting, 167a; general meeting of, 697.

Acetylene, reaction with thiols to form vinyl sulfides, 821; and vinyl ethers, synthesis of sulfur compounds with the aid of, 135.

Acetylenes, monosubstituted, formation by the action of sodium on 2,2-dichlorovinyl derivatives, properties, 923.

Acid, 2-ethylhexanoic, reaction of esters with 2-methylallylmagnesium chloride, 339; ethylphosphonous, esters of, and some of their reactions, 935; styrylphosphonic, diesters of, preparation, properties, 915.

Acids, 2-(2-alkoxyethoxy)vinylphosphonomonodi- and tri-thioic, diesters of, preparation, properties, 911; aminoalkylphosphonic, and esters, acylation of, 957; methylation, 961; carboxylic, of structure $CCl_3(CH_2)$n COOH and CCl_2=CH (CH_2)n COOH, preparation and dissociation constants, 35; ω-chloro carboxylic, preparation, reactions, derivatives, 199; β-chlorostyrylphosphonic, and phenylethynylphosphonic, diesters of, preparation properties, 919; cis- and trans-1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic, lactonization of, 257; dodecanedioic and hexadecanedioic, synthesis, 555; 4-methyl-1,2-cyclohexanedicarboxylic, geometric isomerism of, 265; phosphorodithioic, esters of, preparation, properties, use as insecticides, 597.

Acridine compounds. 9-Acridinecarboxaldehyde phenylhydrazone hydrochloride, effect of the character of the substituent on color in derivatives of, 795; modern electronic theory and the color of arylhydrazones of 9-acridinecarboxaldehyde, 293; preparation Spectrographic investigations of chlorine-substituted phenylhydrazones of 9-acridinecarboxaldehyde hydrochloride in alcoholic hydrogen chloride, 955.

Acrylic acids, 2-acylamino-3-halo-, and their derivatives, preparation, properties, 251.

Acylation, of aminoalkylphosphonic, and aminoalkylphosphonothioic acid, 957.

Adsorption on mercury, of vapors (diethyl ether, acetone, heptane and toluene), 193; (water, methanol), 7.

Adsorptional displacement of butene by water from a catalyst surface, free energy change in, 643.

Agricultural chemistry

Some esters of phosphorodithioic acid as insecticides, 597.

Alanines, N-acyl-2,3-dihalo, preparation, properties, 231; reactions of, 401; N-acyl-3-halo, derivatives of, alkylation and acylation of cysteine and 3,3-dimethylcysteine by,409; 2-hydroxy preparation, properties, reactions, 241.

Alcohols, amino, reaction with acrylic and methacrylic esters of glycols (migrational copolymerization), 845; catalytic amination of, 275; monohydric, reaction with glycerol trivinyl ether, 317; of varying molecular weight, effect of the structural factor on the catalytic decomposition of, 689; secondary, tertiary, reactions with quaternary ammonium salts, 667.

Alkanes, dihalo, formation of a three-dimensional polymer by reaction with poly [ethylenephenyl], 327.

Alkylation, destructive, of benzene with pentane, 451.

Alloys, iron, physicochemical basis of formation of diffusional surface layers on, 715.

Aluminoferrites, calcium, solid solutions of, composition, 887.

Aluminosilicates, reaction with solutions of sodium, calcium and aluminum silicates, 539; sodium, vitreous reaction with caustic alkali solutions, 359.

Amides, bisdialkyl, of 2-alkoxy- and 2-phenoxyvinylphosphonic acids, preparation properties, 591; of 2-(2-alkoxyethoxy) vinylphosphonic acids, preparation, properties, 751.

Amination, catalytic, of alcohols, aldehydes, ketones and ethers, 275.

Amines, organosilicon, cyanoethylation of, 685.

α-Amino acids, esters of, quantitative determination of 2,5-piperazinediones in the products of the polycondensation of, 693; 2-Acylamino-3-haloacrylic acids and their derivatives, 251; acylation and alkylation of 3,3-dimethylcysteine, 53, 61; N-acyl-2,3-dihaloalanines, 231; N-acyl-3-halo-2-hydroxyalanines and their derivatives, 241; alkylation and acylation of cysteine and 3,3-dimethylcystein by derivatives of N-acyl-3-haloalanines, 409; 3,3-dimethylisocystein and its derivatives preparation, 47;

isocysteine and its derivatives preparation, 47;
New method for the synthesis of polypeptides, 619;
Reactions of N-acyl-2,3-dihaloalanines. (Acyloxy)pyruvic acids, 401;
Synthesis of α-acylamino β-thiolastones,613.
Ammonium chloride, systems with $CuCl_2$, $CrCl_3$-H_2O, $FeCl_3$-H_2O, $MnCl_2$-H_2O, interphase partition in, 525.
Analytical Chemistry. Equation for the diffusion current at a dropping electrode taking into account the screening of part of the electrode surface, 373;
Identification of hydrocarbons with the aid of dispersion curves, 805;
Isomerization of ethylcyclopropane on silica gel under the conditions of chromatographic adsorption analysis, 1029;
Quantitative determination of 2,5-piperazinediones in the products of the polycondensation of esters of α-amino acids, 693.
Anisole homologs, photodehydro condensation of, 289.
Anthracene, reaction with 2-chlorovinyl ketones in presence of stannic chloride, 735.
Antimonous acid, esters of, action of bromine chlorine on, 601.
Antimony, organo compounds. Action of some alkoxy compounds on trialkoxy-and dialkoxy-chlorostibines, 385.
Arsenic, organo compounds, primary and secondary, new method for the preparation of 417.
Atomic energy, general meeting of the Division of Chemical Sciences of the USSR Academy of Sciences on the peaceful uses of, 1041.
Atoms and radicals, experimental determination of successive elementary reactions of, 345.
Babinet's principle and the low-angle scattering of x-rays by porous glasses, 19.
Barium chloride, system with barium nitrate, determination of crystallization coefficient of thorium B for, 721.
Barium nitrate, systems with $BaCl_2$, $NaNO_3$, determination of crystallization coefficients of thorium B for, 721.
Benzene, and its closest homologs, high-temperature contact-catalysis reactions in presence of hydrogen at high pressure, 95;
catalytic inertness of amorphous nickel in the hydrogenation of, 633;
chloro, polycondensation with 1,2-chloroethane in presence of aluminum chloride,321;
destructive alkylation with pentane, influence of duration of reaction, temperature and amount of catalyst, 451;
ethyl, reactions in presence of Troshkov clay, 281;
o-dichloro, polycondensation with 1,2-dichloroethane, 1011;
polycondensation with 1,2-dichloroethane, in presence of aluminum chloride, features of chain growth in, 151;
sorption isotherms on active carbons, 531.
Benzoyl peroxide, copolymerization of methyl methacrylate and vinyl caprolactam in presence of, 835;
Biochemistry, Polycondensation of glycine ethyl ether, 1023;
Reactions of mercapto amino acids. 2-Acylamino-3-haloacrylic acids and their derivitives, 251;
Reactions of mercapto amino acids. Acylation and alkylation of 3,3-dimethylcysteine, 53,61;
Reactions of mercapto amino acids. N-Acyl-2,3-dihaloalanines, 231;
Reactions of mercapto amino acids. N-Acyl-3-halo-2-hydroxyalanines and their derivatives, 241;
Reactions of mercapto amino acids. Alkylation and acylation of cysteine and 3,3-dimethylcysteine by derivatives of N-acyl-3-haloalanines, 409;
Reactions of mercapto amino acids. 3,3-Dimethylisocysteine and its derivatives, 47;
Reactions of mercapto amino acids. New method for the synthesis of polypeptides, 619;
Reactions of mercapto amino acids. Reactions of N-acyl-2,3-dihaloalanines. (Acyloxy)-pyruvic acids, 401;
Reactions of mercapto amino acids. Synthesis of α-acylamino β-thiolactones, 613.
Bismuth, radiochemical investigation of spallation and fission reaction products resulting from bombardment with 660-mev protons, 517.
Boron organic compounds. Preparation of the isobutyl esters of phenylpropyl- and butylphenyl borinic acids, 859;
synthesis by reacting organomagnesium compounds with potassium and triethyloxonium fluoborates, 41;
synthesis of dialkylborinic esters with the aid of lithium reagents, 1039;
synthesis of sodium tetraphenylboron, 167
Bromide, 3-buten-1-ynylmagnesium, reaction with halotriphenylsilanes, 159.
Bromine exchange in complex platinum bromides, kinetics of, 895.
1,3-Butadiene, 2,3-dimethyl, hydrogenation in presence of platinum, nickel and palladium, 779,

Butene, adsorptional displacement of, by water from a catalyst surface, free energy change in, 643.
Tert-Butyl hydroperoxide, synthesis, Raman spectrum, optical properties, 661;
peroxide, preparation, optical characteristics, 661.
Isobutyric acid, organosilicon esters of, see esters.
Carbon monoxide, mechanism of formation by oxidation of methane, with the aid of formaldehyde labeled with radioactive carbon, 711.
Carbons, active, surface and sorption properties of. Sorption isotherms for benzene and water vapor, 531.
Catalysis, review of recent work, 557;
contact, of benzene and its closest homologs in presence of hydrogen at high temperature and pressure, 95.
Catalyst, chrome-alumina-magnesia, dehydrogenation of pentane in presence of, 503;
surface, free energy change in the adsorptional displacement of butene by water, from, 643.
Catalysts (aluminosilicate), dependence of the kinetics of decomposition of cyclohexene on the structure of, 1031;
metals of palladium group as, in high-temperature reactions of methylcyclohexane in presence of hydrogen at high pressure, 441;
most effective, for the addition of hydrogen sulfide to vinyl ethers in the direction contrary to Markovnikov's rule, 653;
oxide, (magnesium oxide), effect of the method of making modifying additions (stannic oxide) on the properties of, 879;
Catalytic inertness of amorphous nickel in the hydrogenation of benzene and the dehydrogenation of cyclohexane, 683.
Cellulose, and pectic substances, comparative study of the reactivities of the structural units of, in oxidation reactions with sodium metaperiodate and hydrogen peroxide, 991.
Ceramic chemistry. Role of dissociational activation in the sintering of oxides of elements of variable valency, 725.
Chain growth, during polycondensation, in presence of a catalyst, features of, 151.
Chloramphenicol, synthesis, 391.
Chlorides, alkanesulfenyl, reaction with vinylidene fluoride, 769;
of sodium, calcium and aluminum, reaction of solutions with vitreous sodium silicates and aluminosilicates, 539.
Chlorination, and dehydrochlorination of polychloro compounds containing reactive groups, 207;
of dodecane, 867.
Chloro, poly, compounds, containing reactive groups, chlorination and dehydrochlorination, 207.
Chromium chloride, system with NH$_4$Cl-CrCl$_3$, interphase partition in, 525.
Citraconic anhydride, condensation with cis-1,2, 4a,5,8,8a-hexahydro-4a,7-dimethyl-4-vinylnaphthalene, 429;
condensation with 1-vinylcyclohexene, 67.
Clay, Troshkov, as catalyst for reactions of cyclopentane, ethylcyclopentane, ethylcyclohexane and ethylbenzene, 281.
Clinker, industrial cement, aluminoferrites in, 887.
Color, effect of the character of the substitute on, in derivatives of 9-acridine-carboxaldehyde phenylhydrazone hydrochloride, 795.
Complex compounds, crystal-optical method for determining the structures of, 173.
Condensation, diene, of 1-vinylcyclohexene with citraconic anhydride, 67;
diene, of 1-vinylcyclohexene with dimethyl mesaconate, 77;
poly, of dialdehydes and diketones with diamines and glycols, 841;
poly, peculiar features of chain growth during, in presence of a catalyst, 151.
Coumarin, hydro-, radical, phosphonic esters containing, preparation, properties, 605.
Crystallization coefficient, for the distribution of a thorium B(radioactive lead) salt between a salt melt and crystals of an isomorphous salt, determination of, 721.
Crystallography, crystal-optical method for determining the structures of complex compounds, 173.
Crystals, anomalous mixed, interphase partition in systems containing. Systems NH$_4$Cl-CuCl$_2$-H$_2$O and NH$_4$Cl-CrCl$_3$-H$_2$O, 525.
Cuprous chloride, system with NH$_4$Cl-H$_2$O, interphase partition in, 525.
Cyanoethylation, of organosilicon amines, 685.
Cyclization, dehydro, of piperylene, to cyclopentadiene, influence of catalysts, mechanism of, 785.
Cycloalkyls, polyalkylene, preparation, 1001.
Cyclohexane, catalytic inertness of amorphous nickel in the dehydrogenation of, 683;
derivatives. Geometric isomerism of 4-methyl-1,2-cyclohexanedicarboxylic acids, 265;
ethyl-, reactions in presence of Troshkov clay, 281; methyl, high-temperature reactions of, in a continuous flow system in presence of metals of the palladium group and of hydrogen at high pressure, 441.
Cyclohexene, dependence of the kinetics of decomposition on the structure of the catalyst, 1031;
1-vinyl, condensation with citraconic anhydride, 67;

  1-vinyl, condensation with dimethyl mesaconate, 77.
2-Cyclohexen-1-one, 2-methyl-, condensation with isoprene, 423.
Cyclopentadiene, formation by catalytic dehydrocyclization of piperylene, 785.
Cyclopentane and ethyl derivative, reactions in presence of Troshkov clay, 281.
Cyclopropane, ethyl, isomerization on silica gel under the conditions of chromatographic adsorptional analysis, 1029.
Cysteine, alkylation and acylation by derivatives of N-acyl-3-haloalanines, 409;
  3,3-dimethyl, acylation and alkylation of, 53, 61; 3,3-dimethyl, alkylation and acylation by derivatives of N-acyl-3-haloalanines, 409.
  Isocysteine, 3,3-dimethyl, and derivatives, preparation, 47.
Dearylation of Ar_2PbX_2 as a method of sythesizing a new class of compounds $ArPbX_3$, 633.
Decomposition, catalytic, of alcohols of varying molecular weight, effect of the structural factor on, 689.
Dehydrogenation, catalytic, of isopentane, 869.
Dialdehydes, polycondensation with diamines and glycols, 841.
Diamines, aromatic, conversion to mixed polyamides by reaction with dicarboxylic acids, 487;
  polycondensation with dialdehydes and diketones, 841;
  reaction with acfylic and methacrylic esters of glycols, (migrational copolymerization), 845.
Diketones, polycondensation with diamines and glycols, 841.
Dispersion curves, as an aid to the identification of hydrocarbons, 805.
Dissociation constants, of acids of structure $CCl_3(CH_2)_nCOOH$ and $CCl_2=CH(CH_2)_nCOOH$, 35.
Dodecane, chlorination, 867.
Dumansky, A.V. Salutation on 75th birthday, 343.
Dyestuffs chemistry, Absorption spectra and molecular structure. Effect of the character of the substituent on color in derivatives of 9-acridinecarboxaldehyde phenylhydrazone hydrochloride, 795; Spectroscopic investigations of solutions of chlorine-substituted phenylhydrazones of 9-acridinecarboxaldehyde hydrochloride in alcoholic hydrogen chloride, 983.
Electrode, dropping, equation for the diffusion current at, taking into account the screening of part of the electrode surface, 373.
Electronic theory, and the color of arylhydroazones of 9-acridinecarboxaldehyde, 293.
Epcihlorohydrin, reactions with organochlorosilanes, 469.
Equilibrium, tautomeric, in solution, theory of. Effect of solvation on the equilibrium between the keto and isomeric cis and trans enol forms, 85.
Esters, acrylic, methacrylic, of glycols, reaction with glycols, diamines and amino-alcohols (migrational copolymerization), 845;
  4-alkylsalicylic, formation from alkyl 2-chlorovinyl ketones and ethyl acetoacetate, structure, derivatives, reactions, 729;
  di-, of 2-alkoxy- and 2-phenoxy-vinylphosphonthionic acids, preparation, properties, 595;
  di-, of 2-alkoxy- and 2-phenoxy-vinylphosphonodithiolic and of 2-alkoxy- and 2-phenoxyvinylphosphonotrithioic acids, preparation, properties, 741;
  di-, of 2-(2-alkoxyethoxy)vinyl-phosphonic acids, preparation, properties, 745;
  di-, of 2-(2-alkoxyethoxy)vinylphosphonomono-, di- and tri-thioic acids, preparation, properties, 911;
  di-, of β-chlorostyrylphosphonic and pheyniethynylphosphonic acids, preparation, properties, 919;
  di-, of 2-isopropoxy-, 2-isobutoxy-, and 2-isopentyloxy-vinylphosphonic acids, preparation, properties, 377;
  di-, of 2-phenoxyvinylphosphonic acid, preparation, properties, 383;
  di-, of styrylphosphonic acid, preparation, properties, 915;
  isobutyl, of phenylpropyl- and butylphenyl borinic acids, preparation, 859;
  of α-amino acids, see α-amino acids;
  of 1-aminoalkylphosphonic acids, methylation, 961;
  of antimonous acid, action of halogens on, 601;
  of dialkylphosphinic acids, preparation, properties, 225;
  of 2-ethoxy-, 2-propoxy-, 2-butoxy- and 2-hexyloxy-vinylphosphonic acids, preparation, properties, 213;
  of 1-hydroxyalkylphosphonic acids, preparation, properties, 761;
  of palmitic, and 2-ethylhexanoic acids, reaction with 2-methylallylmagnesium chloride, 339;
  of phosphorodithioic acids, preparation, properties, use as insecticides, 597;
  of polyvinyl alcohol, synthesis, properties, 103;
  of polyvinyl alcohol, with formic, acetic, propionic, butyric and isobutyric acids, physicomechanical properties of, 301;
  organosilicon, of propionic and isobutyric acids, preparation, properties, 465;
  phosphonic, containing a hydorcoumarin radical, preparation, properties, 605;
  triethylphosphonamidous, preparation, properties, 935.

Ethane, 1,2-dichloro, polycondensation with benzene in presence of aluminum chloride, features of chain growth, 151;
  polycondensation with chlorobenzene in presence of aluminum chloride, 321;
  polycondensation with o-dichlorobenzene, 1011;
  polycondensation with toluene, 1007.
Ethanes, bis(alkylthio), bis(arylthio), formation from acetylene and thiols, properties, 821.
Ethanol, 2-anilino, vinyl ether of, preparation, properties, reactions, 127;
  2-diphenylamino, vinyl ether of, preparation, properties, reactions, 829;
  2-vinyloxy, copolymerization with methacrylic acid and methyl methacrylate, 109.
Ethanolamines, vinyl ethers of, preparation, properties, optical investigation, structure, 481;
  synthesis and reactions. Vinyl ether of 2-anilinoethanol, 127.
Ether, 2-bromoethyl phenyl, reactions in presence of zinc chloride and a mixture of zinc and aluminum chloride, 865;
  glycerol trivinyl, reaction with monohydric alcohols, 317;
  glycine ethyl, polycondensation of, in presence of carbon dioxide as catalyst, 1023;
  poly(butyl vinyl), stepwise synthesis of, 121;
  poly(ethyl vinyl), stepwise synthesis of, 309;
  vinyl, of 2-anilinoethanol, preparation, properties, reactions, 127;
  vinyl, of 2-diphenylaminoethanol, preparation, properties, reactions, 829.
Ethers, alkyl vinyl, reaction with glycerol and with glycerol 1,2- and 1,3-cyclic acetals, 313;
  isopropyl vinyl and cyclohexyl vinyl, polymerization in presence of 2,2 -azobis(2-methylpropionitrile), 997;
  vinyl, and acetylene, synthesis of sulfur compounds with the aid of, 135;
  vinyl, copolymerization with methyl acrylate, 115; vinyl, of ethanolamines, preparation, properties, optical investigation, structure, 481;
  vinyl, reaction with diethyl- and diphenylsilanediols, 871;
  vinyl, reaction with pentaerythritol, 477;
  vinyl, the most effective catalysts for the addition of hydrogen sulfide to, in the direction contrary to Markovnikov's rule, 653.
Ethyl acetoacetate, reaction with alkyl 2-chlorovinyl ketones to form 4-alkylsalicylic esters, 729.
Fenchone, reaction with organomagnesium and organolithium compounds, 901.
Ferric chloride, system with NH_4Cl-H_2O, interphase partition in, 525.
Fluoborates, of potassium and triethyloxonium, reaction with organomagnesium compounds, 41.
Formals, preparation, from quaternary ammonium salts and secondary and tertiary alcohols, 667.
Gasoline, Tuimazin, reforming in contact with Troshkov kaolin, 965.
Glass chemistry, reaction of vitreous sodium- and alumino-silicates with salt solutions, 539.
Glasses, porous, Babinet's principle and the low-angle scattering of x-rays by, 19;
  sodium borosilicate, structure of, in relation to the phenomenon of opalescence, 27;
  sodium borosilate, porous, structure of, in relation to phenomenon of opalescence, 177;
  sodium borosilicate, structure of, in its relation to the phenomenon of opalescence, 353;
  sodium silicate and aluminosilicate, reaction with caustic alkali solutions, 359.
Glycerol, reaction with alkyl vinyl ethers, 313;
  1,2- and 1,3-cyclic acetals, reaction with alkyl vinyl ethers, 313.
Glycidol, reactions with organochlorosilanes, 469.
Glycols, polycondensation with dialdehydes and diketones, 841.
Halides, 2-alkenyl, conversion to branched aliphatic hydrocarbons, 571;
  alkyl, behavior in condensation reactions with 3-, 4-, and 5-alkenyl halides in presence of magnesium 459;
  3-,4-, and 5-alkenyl, behavior in condensation reactions with alkyl halides in presence of magnesium, 459.
Halogens, (chlorine, bromine), action on esters of antimonous acid, 601.
High polymer chemistry. Comparative study of the reactivities of the structural units of cellulose and pectic substances in oxidation reactions with sodium metaperiodate and hydrogen peroxide, 991;
  Dependence of the properties of aliphatic polyamides having "even" repeating units on the structure of the repeating unit, 673;
  Dependence of the properties of aliphatic polyamides having "odd" repeating units on the structure of the repeating unit, 679;
  Determination of the molecular weights of polyamides from the viscosities of their solutions in cresol and in methanol, 1017;
  Macromolecular compounds. A case of migrational copolymerization, 845;
  Macromolecular compounds. Dependence of the properties of polyamides on the extent of intermolecular hydrogen bonding, 143;
  Macromolecular compounds. Dependence of the properties of polyamides on the extent of intermolecular hydrogen bonding, 493;

  Macromolecular compounds. Effect of aromatic components on the properties of mixed polyamides, 487;
  Macromolecular compounds. Formation of a three-dimensional polymer by reaction of poly-(ethylenephenyl) with dihaloalkanes, 327;
  Macromolecular compounds. Mixed polyamides containing glutaric or pimelic acid resudues, 849;
  Macromolecular compounds. Peculiar features of chain growth during polycondensation in presence of a catalyst, 151;
  Macromolecular compounds. Polycondensation of 1,2-chloroethane with chlorobenzene of aluminum chloride, 321;
  Macromolecular compounds. Products of the polycondensation of dialdehydes and diketones with diamines and glycols, 841;
  Macromolecular compounds. Role of exchange reactions in polyamide formation, 499;
  Macromolecular compounds. Some two-component mixed polyamides, 333;
  Macromolecular compounds. Synthesis of polyalkylenecycloalkyls, 1001;
  Macromolecular compounds. 2,4,5-triisopropyl-α-methylstyrene, 855;
  Polycondensation of 1,2-dichloroethane with o-dichlorobenzene, 1011;
  Polycondensation of 1,2-dichloroethane with toluene, 1007;
  Polycondensation of glycine ethyl ether, 1023,
  Polymerization of isopropyl vinyl and cyclohexyl vinyl ethers in presence of 2,2'-azobis (2-methylpropionitrile), 997;
  Polymerization of vinyl compounds. Stepwise synthesis of poly(butyl vinyl ether), 121;
  Polymerization of vinyl compounds. Stepwise synthesis of poly (ethyl vinyl ether), 309;
  Reactions of unsaturated and macromolecular compounds. Copolymerization of methyl acrylate and vinyl ethers, 115;
  Reactions of unsaturated and macromolecular compounds. Copolymerization of some vinyl compounds with 2.-vinyloxyethanol, 109;
  Reactions of unsaturated and macromolecular compounds. Copolymerization of vinylcaprolactam with methyl methacrylate in presence of benzoyl peroxide and of 2,2' -azobis (2-methylpropionitrile), 835;
  Some physico-mechanical properties of esters of polyvinyl alcohol, 301;
  Synthesis of 2,2'-azobis (2-methylpropionitrile) labeled with radioactive carbon (C^{14}), 555;
  Synthesis of esters of polyvinyl alcohol, 103.
Hydrocarbons, aromatic, high-temperature contact catalysis of, in presence of hydrogen at high pressure, 95;
  branched chain aliphatic, synthesis via 2-alkenyl halides, 571;
  identification of, with the aid of dispersion curves, 805;
  reactions in contact with natural aluminosilicates, 281.
Hydrogenation, of 2,3-dimethyl-1,3-butadiene in presence of platinum, nickel and palladium, 779.
Hydrogen bonding, intermolecular, dependence of properties of mixed polyamides on, 493;
  intermolecular, in mixed polyamides, graphical method for the determination of, dependence of properties of polyamides on, 149.
Hydrogen peroxide, at high concentration, systems containing. Thermal stability of urea perhydrate, 705;
  synthesis of tert-butyl hydroperoxide and tert-butyl peroxide and their optical investigation in relation to the problem of the structure of, 661; system with LiOH-H_2O, solubility isotherms and polytherms, 365;
  system with NaOH-H_2O, thermal characteristics and stabilities of, 187;
  ternary system with NaOH-H_2O, 0° isotherm for, 15.
Hydrogen sulfide, most effective catalysts for the addition of vinyl ethers in the direction contrary to Markovnikov's rule, 653.
Insecticides, esters of phosphorodithioic acids as, 597.
Ions, in solution, relation between the mobilities of, and their self-diffusion coefficients, 513.
Iron, and its alloys, physicochemical basis of formation of diffusional surface layers on, 715.
Isomerization, of ethylcyclopropane on silica gel under the conditions of chromatographic adsorption analysis, 1029.
Isopentane, catalytic dehydrogenation of, 869.
Isoprene, condensation with 2-methyl-2-cyclohexen-1-one, 423.
Isotopes, radioactive, isolated in the bombardment of bismuth with 660-Mev protons, 517.
Kaolin, Troshkov, as catalyst for the reforming of Tuimazin gasoline, 965.
Keto-enol tautomerism, equilibrium in solution, 85.
Ketones, alkyl, 2-aminovinyl, synthesis, 157;
  alkyl, 2-chlorovinyl, reaction with ethyl acetoacetate, to form 4-alkyl-salicylic esters, 729;
  alkyl, 2-phenoxyvinyl, chemical reactions of, 579; 2-chlorovinyl, reaction with anthracene (diene synthesis), 735.
β-Lactams, new method of preparation from amides of β-halocarboxylic acids, 951.
Lactones, α-acylamino, β-thio, synthesis properties, reactions, 613;
  thio, of β-mercapto carboxylic acids, preparation, properties, derivatives, 507.
Lactonization of cis-and trans-1,2,3,5,6,7,8,8a-octa-

hydro-1,2-naphthalene-dicarboxylic acids, 257.

Lead organic compounds, preparation, properties. Compounds of the classes Ar_2PbX_2 and $ArPbX_3$ in the p-tolyl series, 639;
preparation, properties. Dearylation of Ar_2PbX_2 as a method of synthesizing a new class of compounds $ArPbX_3$, 633.

Lithium hydroxide, system with H_2O_2-H_2O, solubility isotherms and polytherms, 365.

Lithium organic compounds, reaction with fenchone, 901; use in the preparation of dialkylborinic esters, 1039.

Lithium oxide, system with Li_2O_2, physicochemical properties of, 545.

Lithium peroxide, system with Li_2O, physicochemical properties of, 545.

Magnesium, behavior of 3-,4-, and 5-alkenyl halides in presence of, in condensation reactions with lakyl halides, 459.

Magnesium organo compounds. Allylmagnesium chloride, 2.methyl, reaction with esters of palmitic and 2-ethylhexanoic acids, 339;
Reaction of 3-buten-1-ynylmagnesium bromide with halotriphenylsilanes, 159;
reaction with fenchone, 901;
reactions with potassium and triethyloxonium fluoborates, 41.

Manganese chloride, system with NH_4Cl-H_2O, interphase partition in, 525.

Markovnikov's rule, most effective catalysts for the addition of hydrogen sulfide to vinyl ethers in the direction contrary to, 653.

Medicinal chemistry. New method of preparing β-lactams, 951;
Reactions of mercapto amino acids. Alkylation and acylation of cysteine and 3,3-dimethylcysteine by derivatives of N-acyl-3-haloalanines, 409;
Reactions of mercapto amino acids. New method for the synthesis of polypeptides, 619;
Reactions of mercapto amino acids. Reactions of N-acyl-2,3-dihaloalanines. (Acyloxy)pyruvic acids, 401;
Reactions of mercapto amino acids. Synthesis of α-acylamino β-thiolactones, 613;
Synthesis of chloramphenicol, 391;
Synthesis of steroid compounds and related substances. Condensation of isoprene with 2-methyl-2-cyclohexen-1-one. Synthesis of cis-1,2,4a,5,8,8a-hexahydro-4a,7-dimethyl-4-vinylnaphthalene, 423.

Mercapto amino acids, see amino acids, mercapto

Mercury compounds, symmetrical aromatic, reaction with phenols, 975.

Mercury surface, adsorption of vapor (diethyl ether, acetone, heptane and toluene) at, 193;
adsorption of vapor (water, methanol)., at, 7.

Mesaconate, dimethyl, condensation with 1-vinylcyclohexene, 77.

Metallurgical chemistry. Physicochemical basis of the formation of diffusional surface layers on iron and its alloys, 715.

Methacrylic acid, copolymerization with 2-vinyloxyethanol, 109.

Methane, mechanism of oxidation of, with the aid of labeled atoms, 711.

Methanol vapor, adsorption at a mercury surface, 7.

Methyl acrylate, copolymerization with vinyl ethers, 115.

Methylation, of 1-aminoalkylphosphonic acids and their esters, 961.

Methyl methacrylate, copolymerization, with vinyl caprolactam in presence of benzoyl peroxide and of 2,2'-azobis(2-methylpropionitrile), 835;
copolymerization, with 2-vinyloxyethanol, 109.

Molecular weights, of polyamides, determination from the viscosities of their solutions in cresol and in methanol, 1017.

Morpholinone, 3-thia, derivatives of, formation by S-alkylation of 3,3-dimethylcysteine, 53.

Naphthalene compounds. Condensation of cis-1,2,4a,5,8,8a-hexahydro-4a, 7-dimethyl-4-vinylnapthalene with citraconic anhydride, 429;
Lactonization of cis- and trans-1,2,3, 5,6,7,8,8a-octahydronapthalenedicarboxylic acids, 257;
Synthesis of cis-1,2,4a,5,8,8a-hexahydro-4a,7-dimethyl-4-vinylnapthalene, 423.

Nickel, amorphous, catalytic inertness of, in the hydrogenation of benzene and the dehydrogenation of cyclohexane, 683.

Nylon, melting points, 673.

Olefins, perfluoro, addition reactions of. Addition of sulfur chlorides, 627;
perfluoro, addition reactions of. Reaction of vinylidene fluoride with sulfur chlorides and with alkanesulfenyl chlorides, 769.

Opalescence, of sodium borosilicate glasses, and relationship with structure, 353;
of sodium borosilicate glasses, in relation to structure, 27;
structure of porous sodium borosilate glasses and the phenomenon of, 177.

Oxazolinones, preparation, 237, 248,251.

Oxidation, of sodium polygalacturonate by means of molecular oxygen, sodium metaperiodate and hydrogen peroxide, 815;
reactions, of pectic substances, of cellulose, and of the structural units of these substances, 815;
reactions with sodium metaperiodate and hydrogen peroxide, with cellulose and pectic substances, comparative study of the reactivities of the structural units of, 991.

Oxides, of elements of variable valency (copper, iron and manganese oxides), role of dissociational activation in the sintering of, 725.
Oxygen, influence on sintering of oxides of variable valency (copper, iron and manganese oxides), 725.
Palmitic acid, esters of, reaction with 2-methylallylmagnesium chloride, 339.
Parachors, of trialkylmethylsilanes, 945.
Partition, interphase, in systems containing anomalous mixed crystals. systems NH_4Cl-$CuCl_2$-H_2O and NH_4Cl-$CrCl_3$-H_2O, 525.
Pectic substances and cellulose, comparative study of the reactivities of the structural units of, in oxidation reactions with sodium metaperiodate and hydrogen peroxide, 991.
Pentaerythritol, reaction with vinyl ethers, 477.
Pentane, catalysis reactions (dehydrogenation), in presence of a chrome-alumina-magnesia catalyst, influence of temperature, 503;
  destructive alkylation of benzene with, 451.
Pentanol, 3,3,4-trimethyl, preparation, properties, reactions, 969.
Peptides, formation, quantitative determination of 2,5-piperazinediones in the presence of, 693;
  poly, new method for the synthesis of, 619.
Petroleum chemistry. Destructive alkylation of benzene with pentane, 451;
  Reforming of Tuimazin gasoline in contact with Troshkov kaolin, 965.
Phenazine, dimetal compounds of, preparation, properties, structure, 775.
Phenols, reactions with symmetrical aromatic mercury compounds, 975.
Phosphinic acids, dialkyl, esters of, preparation, properties, 225.
Phosphites, alkyl bis 1-(diethoxyphosphinyl) alkyl preparation, properties, 929.
Phosphonic acid, 1-hydroxyalkyl, derivatives of, preparation, properties, 761.
Phosphonic acids, esters of, containing a hydrocoumarin radical, preparation, properties, 605;
  unsaturated, derivatives of. Bisdialkylamides of 2-alkoxy- and 2-phenoxy-vinyl-phosphonic acids, 591;
  unsaturated, derivatives of. Bisdialkylamides of 2-(2-alkoxyethoxy)vinylphosphonic acids, preparation, properties, 751;
  unsaturated, derivatives of. Diesters of 2-alkoxy- and 2-phenoxy-vinylphosphonothionic acids, 595;
  unsaturated, derivatives of. Diesters of 2-alkoxy- and 2-phenoxy-vinyl-phosphonodithiolic and of 2-alkoxy- and 2-phenoxy-vinylphosphonotrithioic acids, 741;
  unsaturated, derivatives of. Diesters of 2-(2-alkoxyethoxy)vinylphosphonic acids, preparation, properties, 745;
  unsaturated, derivatives of. Diesters of 2-(2-alkoxyethoxy)vinylphosphonomono-, di-, and tir-thioic acids, 911;
  unsaturated, derivatives of. Diesters of 2- isopropoxy-, 2-isobutoxy-, and 2-isopentyloxyvinylphosphonic acids, preparation, properties, 377;
  unsaturated, derivatives of. Diesters of 2-phenoxyvinylphosphonic acid, preparation, properties, 383;
  unsaturated, Derivatives of. Diesters of styrylphosphonic acid, 915;
  unsaturated, derivatives of. Esters of 2-ethoxy-, 2-propoxy-, 2-butoxy- and 2-hexyloxyvinylphosphonic acids, preparation, properties, 213.
Phosphorodichloridites, alkyl, products of reaction with sodium diethyl phosphorothionate, 221.
Phosphorothionate, sodium diethyl, products of reaction with phosphorodichloridites, 221.
2,5-Piperazinediones, quantitative determination of, in the products of the polycondensation of esters of α-amino acids, 693.
Piperylene, catalytic dehydrocyclization to cyclopentadiene, influence of catalysts, mechanism of, 785.
Platinum, quadrivalent, complex compounds of, determination of structure by crystal-optical methods, 173.
  Platinum bromides, complex, bromine exchange in, 895.
Polarography, Equation for the diffusion current at a dropping electrode taking into account the screening of part of the electrode surface, 373.
Polyamide formation, role of exchange reactions in, 499.
Polyamides, aliphatic, having "even" repeating units, dependence of properties on the structure of the repeating unit, 673;
  aliphatic, having "odd" repeating units, dependence of properties on the structure of the repeating unit, 679;
  determination of molecular weights of, from the viscosities of their solutions in cresol and in methanol, 1017;
  dependence of properties on the extent of intermolecular hydrogen bonding, 143;
  mixed, containing glutaric or pimelic acid residues, preparation, properties, 849;
  mixed, dependence of properties on the extent of intermolecular bonding, 493;
  mixed, effect of aromatic components on the properties of, 487;

two-component mixed, preparation, properties, 333.
Poly ethylenephenyl formation of a three-dimensional polymer by reaction with dihaloaklanes, 327.
Polymerization, migrational, reaction of acrylic and methacrylic esters of glycols with glycols, diamines and aminoalcohols, 845.
polyvinyl alcohol, esters of, see esters.
Propene, 3,3,3-trichloro, condensation with aromatic compounds (bromobenzene, chlorobenzene and anisole, phenol), 906.
Propionic acid, organosilicon esters of, see esters.
Propionitrile, 2,2'-azobis-2-methyl, as catalyst for the polymerization of isopropyl vinyl and cyclohexyl vinyl ethers, 997;
2,2'-azobis 2-methyl methacrylate and vinyl caprolactam in presence of, 835;
2,2'-azobis(2-methyl) labeled with radioactive carbon (C^{14}), synthesis, 555.
Pyridinium salts, 1-(alkoxymethyl), reactions with secondary and tertiary alcohols, 667.
Pyruvic acids (acyloxy), preparation, properties, 401.
Quaternary ammonium salts, exchange and cleavage reactions of. Reactions with secondary and tertiary alcohols, 667.
Radicals and atoms, experimental determination of the sequence of successive elementary reactions of, 345.
Radioactive chemistry. Determination of the crystallization coefficient for the distribution of a thorium B (radioactive lead) salt melt and crystals of an isomorphous salt, 721;
Study, with the aid of labeled atoms, of the reaction mechanism of the oxidation of methane. Mechanism of the formation of carbon monoxide, 711.
Radioactive isotopes, see isotopes.
Reactions, elementary, successive, of atoms and radicals, experimental determination of sequence of, 345.
Refractive indices, method for recording of, in the U.V. region of the spectrum, 805.
Silanes, 3- and 4-alkenyltrialkyl, synthesis, properties, 161;
(1-cyano-1-methylethoxy), preparation, properties, 1035;
halotriphenyl, reaction with 3-buten-1-ynylmagnesium bromide, 159;
organochloro, reactions with epichlorohydrin and glycidol, 469;
trialkylmethyl, preparation, properties, parachors of, 945.
Silicates, field of solid solutions formed by celsian, diabarium trisilicate, and barium disilicate (sanbornite), 1;
sodium, vitreous, reaction with caustic alkali solutions, 359;
sodium, vitreous, reaction with solutions of sodium, calcium and aluminum chlorides, 539.
Silicon organic compounds, containing oxygen, synthesis and reactions of. Reactions of diethyl- and diphenyl- silanediols with vinyl ethers, 871;
Cyanoethylation of organosilicon amines, 685;
Synthesis of 1,1-dichlorosilacyclopent-3-ene, properties, 861.
Silicon, orgno-, esters, see esters.
Sintering, of oxides of elements of variable valency (copper, iron and manganese oxides), role of dissociational activation in, 725.
Sodium, action on compounds containing a $CCl_2=CH$ group (2,2-dichlorovinyl derivatives), 923;
borosilicate glasses, see glasses, sodium borosilicate;
hydroxide, system with hydrogen peroxide-water, thermal characterisitics and stabilities of, 187;
hydroxide, ternary system with H_2O_2–H_2O, 0° isotherm for, 15;
nitrate, system with $Ba(NO_3)_2$, determination of crystallization coefficient of thorium B for, 721;
polygalacturonate, oxidative degradation of, by means of molecular oxygen, sodium metaperiodate, and hydrogen peroxide, 815.
Solutions, aqueous, reaction with vitreous sodium silicates and aluminosilicates, 359;
(sodium, calcium and aluminum chlorides) reaction with vitreous sodium silicates and solid aluminosilicates, 539;
olid, ternary, formed by barium disilicate, dibarium trisilicate, and celsian, boundaries of field of, study of liquidus surface, 1.
Solvation, effect on the equilibrium between the keto and isomeric cis and trans enol forms, 85.
Sorption, of benzene and water vapor on active carbons, 531.
Spectra, absorption, and molecular structure. Effect of the character of the substituent on color in derivatives of 9-acridine-carboxaldehyde phenylhydrazone hydorchloride, 795;
absorption, and molecular structure. Modern electronic theory and the color of arylhydrazones of 9-actidinecarboxaldehyde, 293;
absorption, and molecular structure. Spectroscopic investigations of solutions of chlorine-substituted pheynylhydrazones of 9-acridine-carboxaldehyde hydrochloride in alcoholic hydrogen chloride, 983.
Stereochemistry of cyclic compounds. Condensation of cis-1,2,4a,5,8,8a-hexahydro-4a,7-dimethyl-4-vinylnaphthalene with citraconic anhydride, 429;
Condensation of 1-vinylcyclohexene with citraconic

anhydride, 67;
Condensation of 1-vinylcyclohexene with dimethyl mesaconate, 77;
Geometric isomerism of 4-methyl-1,2-cyclohexenedicarboxylic acids, 265;
Lactonization of cis- and trans-1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acids,257.
Steroid compounds, and related substances, synthesis of, Condensation of, Condensation of isoprene with 2-methyl-2-cyclohexen-1-one. Synthesis of cis-1,2,4a,5,8,8a-hexahydro-4a,7-dimethyl-4-vinylnaphthalene, 423.
Stibines, trialkoxy-, and dialakoxychloro-, action of some alkoxy compounds on, 385.
Styrene, 2,4,5-triisopropyl-α-methyl, preparation, reactions, 855.
Sulfide, ethyl vinyl, ion-catalyzed reactions of, with water, with ethanol, with Hcl and with HBr, 135.
Sulfides, vinyl, general method for the synthesis of, by reacting thiols with excess acetylene, properties, cleavage, 821.
Sulfur chlorides, addition to perfluoroolefins, 627;
reaction with vinylidene fluoride, 769.
Sulfur compounds, synthesis by the aid of vinyl ethers and acetylene. The most effective catalysts for the addition of hydrogen sulfide to vinyl ethers in the direction contrary to Markovnikov's rule, 653;
synthesis with the aid of vinyl ethers and acetylene. Ion-catalyzed reactions of ethyl vinyl sulfide, 135.
Surface layers, diffusional, physicochemical basis of formation of, on iron and its alloys, 715.
Synestrol, photosynthesis of, 289.
System, $CO(NH_2)_2$-H_2O_2—H_2O, thermal stability of urea perhydrate, 705;
Li_2O_2-Li_2O, physicochemical properties of, 545;
NaOH-H_2O_2-H_2O, thermal characteristics and stabilities of solid phases of, 187;
NH_4Cl-$CrCl_3$-H_2O, interphase partition in, 525;
NH_4Cl-$CuCl_2$-H_2O, interphase partition in, 525;
ternary, LiOH-H_2O_2-H_2O, solubility isotherms and polytherms, 365.
Systems, binary, $Ba(NO_3)_2$-$BaCl_2$, -$NaNO_3$, crystallization of thorium B for, 721;
containing hydrogen peroxide at high concentration. 0° isotherm of the ternary system NaOH-H_2O_2-H_2O, 15.
Tautomeric equilibrium, see equilibrium.
p-Terpheynyl, preparation, by dehydrogenation of p-dicyclohexylbenzene with selenium, 857.
Thiols, reaction with excess acetylene, to form vinyl sulfides, 821.
Thiophene compounds. Synthesis and reactions of 2,2'-methylendithiophene derivatives, 509.
Thorium B(radioactive lead) salt, crystallization coefficient for the distribution between a salt melt and crystals of an isomorphous salt, 721.
Titanium organic compounds. Synthesis of alkoxybromotitaniums and alkoxychloropolytitanoxanes, 755.
Toluene, polycondensation with 1,2-dichloroethane, 1007.
Trofimov, Alekandr Vasilyevich, obituary notice,875.
Unsaturated compounds having a conjugated system of double bonds, catalytic hydrogenation of. Hydrogenation of 2,3-dimethyl-1,3-butadiene in presence of platinum, nickel and palladium,779.
Urea, system with H_2O_2-H_2O, thermal stability of urea perhydrate, 705.
Vapors, adsorption on mercury, (diethyl ether, acetone, heptane and toluene), 193;
adsorption on mercury (water, methanol), 7.
Vinyl alcohol, poly, esters of, see esters;
caprolactan, copolymerization with methyl methacrylate in presence of benzoyl peroxide and of 2,2'-azobis[2-methypropionitrile] 835; compounds (methacrylic acid and methyl methacrylate), copolymerization with 2-vinyloxyethanol, 109;
compounds, polymerization of; stepwise synthesis of poly [ethyl vinyl ether], 309;
compounds, reactions with multifunctional compounds. Reaction of alkyl vinyl ethers with glycerol and with glycerol 1,2- and 1,3-cyclicacetals,313;
compounds, reactions with multifunctional compounds. Reaction of glycerol trivinyl ether with monhydric alcohols, 317;
compounds, reaction with multifunctional compounds. Reaction of vinyl ethers with pentaerythritol, 477;
2,2-dichloro-, derivatives, action of sodium,923.
Vinylidene fluoride, reaction with sulfur chloride and with alkanesulfenyl chlorides, 769.
Vinylphosphonic acids, see phosphonic acids.
Viscosities of cresol and methanol solutions of polyamides, and determination of molecular weight, 1017.
Water, system with H_2O_2-$CO(NH_2)_2$, thermal stability of urea perhydrate, 705;
system with LiOH-H_2O_2, solubility isotherms and polytherms, 365;
ternary system with NaOH-H_2O_2, 0° isotherm for, 15;
vapor, adsorption at a mercury surface, 7;
vapor, sorption isotherms on active carbons, 531.
X-rays, low-angle scattering of, by porous glasses, and Babinet's principle, 19.

FIELD OF SOLID SOLUTIONS FORMED BY CELSIAN, DIBARIUM TRISILICATE, AND BARIUM DISILICATE (SANBORNITE)

N. A. Toropov, F. Ya. Galakhov and I. A. Bondar

The study of ternary solid solutions in the three-component system $BaO-Al_2O_3-SiO_2$ presents great interest. In silicate systems, as also in metal systems, cases in which binary solid solutions are formed are very numerous. Earlier investigations of the binary system $BaO-SiO_2$ [1], which is included in the ternary system $BaO-Al_2O_3-SiO_2$ with which we are now concerned, indicated the existence of a continuous series of solid solutions formed between two intermediate compounds, dibarium trisilicate ($2BaO \cdot 3SiO_2$) and sanbornite ($BaO \cdot 2SiO_2$). No data existed, however, concerning the behavior of alumina when added to this binary solid solution.

Only comparatively recently Thomas [2] has noted that alumina dissolves in the binary solid solution $BaO \cdot 2SiO_2 - 2BaO \cdot 3SiO_2$, i.e., forms a ternary solid solution between celsian ($BaO \cdot Al_2O_3 \cdot 2SiO_2$), sanbornite ($BaO \cdot 2SiO_2$), and dibarium trisilicate ($2BaO \cdot 3SiO_2$). Attention must be drawn, however, to a certain inconsistency between the binary vertical sections $2BaO \cdot 3SiO_2 - BaO \cdot Al_2O_3 \cdot 2SiO_2$ and $BaO \cdot 2SiO_2 - BaO \cdot Al_2O_3 \cdot 2SiO_2$ given by the author and the values of the refractive indices of the crystals separated in this field.

The sections indicate that celsian has limited solubility both in sanbornite and in dibarium trisilicate, whereas the variation in refractive index presents a picture of an unlimited series of solid solutions between these phases. The author takes the refractive index of celsian as equal to that of the limiting solid solution. For example, at a composition of 50% $BaO \cdot 2SiO_2$ and 50% $BaO \cdot Al_2O_3 \cdot 2SiO_2$, at which, according to the diagram, celsian should be observed as the primary phase, Thomas noted the presence only of a solid solution of refractive index $n_g = 1.600$ and $n_p = 1.588$. Actually, however, this refractive index is characteristic not of a solid solution, but of pure celsian.

EXPERIMENTAL

The object of our work was the detailed verification of the existence of a field of ternary solid solutions, the establishment of the boundaries of this field, and the study of its liquidus surface. We have studied a field that is contiguous with the line $2BaO \cdot 3SiO_2 - BaO \cdot 2SiO_2$, and also with part of the field of barium metasilicate ($BaO \cdot SiO_2$), sanbornite ($BaO \cdot 2SiO_2$), and celsian ($BaO \cdot Al_2O_3 \cdot 2SiO_2$) (Fig. 1).

In the synthesis of the samples the following materials were used: 1) silica, as a fine powder prepared from rock crystal (99.9% SiO_2); 2) concentrated alumina (total impurity 0.2%); 3) barium carbonate ("chemically pure", containing 99.95% $BaCO_3$). Homogeneity was attained in the samples by melting them in an electric arc. The necessary amounts of the original materials were weighed out on an analytical balance and carefully mixed by being ground together in a mortar. The mixture was moistened with a solution of dextrin and formed into rods, 3-4 mm in diameter, with the aid of a glass tube. The samples were dried, and then fused in the electric arc.

The investigation was carried out by the quenching method, the samples being examined microscopically and subjected to X-ray analysis.

The optical study was carried out mainly by the immersion method; in certain cases combined slides were made for transmitted and reflected light. Preliminary observations showed that for all of the compositions studied the initial crystallization temperatures were about 1450°. A platinum furnace was, therefore, used, except for some samples containing a large amount of alumina (over 10%), for which a platinum-rhodium (20% Rh) furnace was used, since the temperature at which the primary phase separated was higher than 1450°.

TABLE

Composition (% by wt.) BaO	Al$_2$O$_3$	SiO$_2$	Temperature of liquidus (°C)	Refractive indices of glasses	Primary phase	Refractive indices of crystals n_g	n_p	mean
52	3	45	1315	1.587	BaO · 2SiO$_2$	1.621*	1.597*	1.609*
55	3	42	1350	1.600	Solid solution	1.619	1.597	1.608
58	3	39	1360	1.613	" "	1.628	1.605	1.616
61	3	36	1375	1.626	" "	1.634	1.609	1.622
64	3	33	1380	1.639	BaO · SiO$_2$	1.678	1.673	1.675
49	6	45	1285		BaO · 2SiO$_2$			
52	6	42	1320	1.595	Solid solution	1.616	1.593	1.604
55	6	39	1330	1.607	" "	1.627	1.604	1.614
58	6	36	1340	1.617	" "	1.632	1.608	1.619
61	6	33	1350		BaO · SiO$_2$			
46	9	45	1240		BaO · 2SiO$_2$			
49	9	42	1275	1.586	Solid solution	1.604	1.589	1.597
52	9	39	1300	1.598	" "	1.611	1.594	1.603
55	9	36	1310	1.610	" "	1.616	1.600	1.608
58	9	33	1320		BaO · SiO$_2$			
43	12	45	1380		BaO · Al$_2$O$_3$ · 2SiO$_2$			
46	12	42	1405	1.578	The same	1.600*	1.588*	1.594*
49	12	39	1430		"			
52	12	36	1450		"			
55	12	33	1475		"			

* Eskola's data [1].

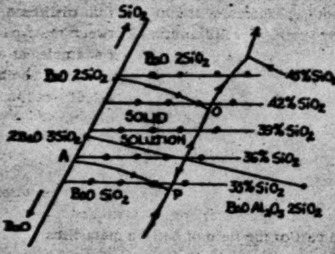


Fig. 1. Field of ternary solid solutions.

As investigation showed (Fig. 1), a field of solid solutions occurs in the ternary diagram, and they contain up to about 10% Al$_2$O$_3$. At a higher alumina content we reach the field of the primary crystallization of celsian. The positions of the boundary lines of the field of ternary solid solutions with barium metasilicate on the one side (A—P) and solid solution and barium disilicate (BaO · 2SiO$_2$—O) on the other are identical with those indicated by Thomas. The points P and O on the diagram are invariant, the point P being a eutectic of melting point 1320°, and point O a reaction point, melting point 1280°. When the limits of the field of solid solutions in the ternary system had been defined, the optical properties of the glasses and separated crystals were examined.

The results of the quenching of the samples investigated, with indications of the liquidus temperature, the nature of the primary phase, and the refractive indices of the glass, are given in the table.

The results of the optical investigation of the glasses showed that with increase in the contents of alumina and barium oxide the refractive index increases, and with increase in the silica content it diminishes. The refractive index of crystals of solid solution formed from the barium silicates 2BaO · 3SiO$_2$ and BaO · 2SiO$_2$ at a constant alumina content changes as the ratio of the amounts of these silicates changes, diminishing from 2BaO · 3SiO$_2$ to BaO · 2SiO$_2$. Reduction in the refractive index is observed also for a constant ratio of the silicates, but increasing amounts of silica (Fig. 2). This is characterized by reduction in the birefringence of the crystals.

In the field studied, therefore, we find changes in optical properties along two directions: along lines parallel to the side BaO—SiO$_2$, and along lines passing from this side to the central part of the triangle. Such a change in the optical properties of the crystals separating can be explained only on the assumption that they are formed from three components. Change in the refractive indices of the primary phases, in their dependence on composition, are shown graphically in Figures 2 (a) and 2 (b). In Fig. 2 (a), the variation of the index n_g with composition is shown, and in Fig. 2 (b) —the change of n_p with composition. The refractive indices for BaO · 2SiO$_2$ and BaO · SiO$_2$ are constant, and are represented by horizontal lines.

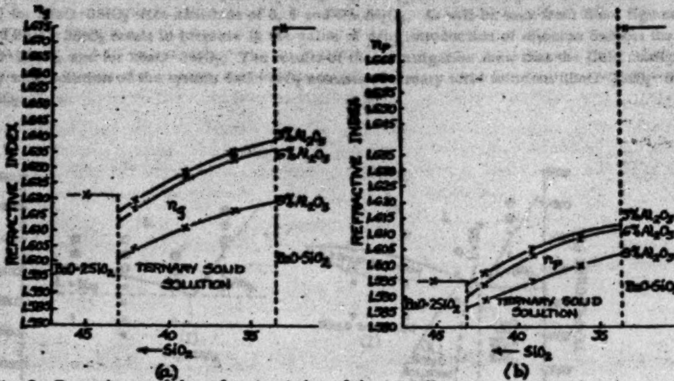


Fig. 2. Dependence of the refractive index of the initially separating crystals on composition for sections of constant alumina content (3, 6 and 9%): a) change in $\underline{n_g}$; b) change in $\underline{n_p}$.

The microscopy results are presented in the microphotographs in Figures 3-12.* Fig. 3 shows crystals of barium disilicate. The microstructures of ternary solid solutions containing 3 and 6% Al$_2$O$_3$ at different temperatures are shown in Figures 4-8: reduction in the temperature from which quenching occurs leads to increased tendency to crystallize and to separation of crystals in the form of fine grains with preservation of homogeneity. The crystallization of a solid solution with simultaneous formation of rectangular plates and needles of celsian having feeble birefringence is shown in Figures 9 and 12 (the photograph in Fig. 12 was obtained with a combined section in reflected light). Rounded grains of barium metasilicate in glass and elongated plates of solid solution are shown in Fig. 10.

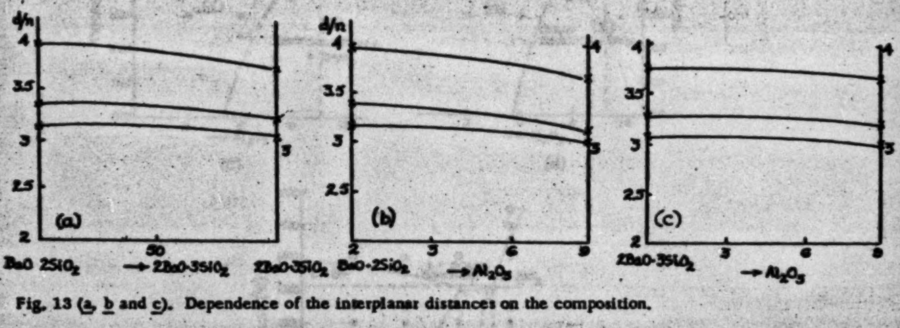


Fig. 13 (a, b and c). Dependence of the interplanar distances on the composition.

An X-ray investigation provided confirmation of the formation of ternary solid solutions; it was carried out with the aid of Co and K α,β radiation in cylindrical cameras, 57.3 mm in effective diameter. Increase both in the alumina content and also in the barium disilicate content caused a displacement of the lines in the X-ray picture with respect to those of the original sample of 2BaO·3SiO$_2$, which is to be explained by the formation of a ternary solid solution of the replacement type.

*** Figures 3-12 are to be found on the plate, page**

Fig. 13 shows the dependence of the interplanar distances (d/n) of various samples on composition: Fig. 13 (a) gives the dependence for the series $BaO \cdot 2SiO_2$—$2BaO \cdot SiO_2$; Fig. 13 (b) for $BaO \cdot SiO_2$ with additions of 3, 6 and 9% Al_2O_3; Fig. 13 (c) for $2BaO \cdot 3SiO_2$ with additions of 3, 6 and 9% Al_2O_3. As will be seen from these figures, additions of $BaO \cdot 2SiO_2$ and $2BaO \cdot 3SiO_2$ result in increase in the value of d/n; introduction of alumina reduces the value of d/n, both for $BaO \cdot 2SiO_2$, and for $2BaO \cdot 3SiO_2$. The results of the investigation show that the field contiguous with the line of binary solid solution of the system BaO—SiO_2 consists of ternary solid solutions $2BaO \cdot 3SiO_2$—$BaO \cdot 2SiO_2$—$BaO \cdot Al_2O_3 \cdot 2SiO_2$.

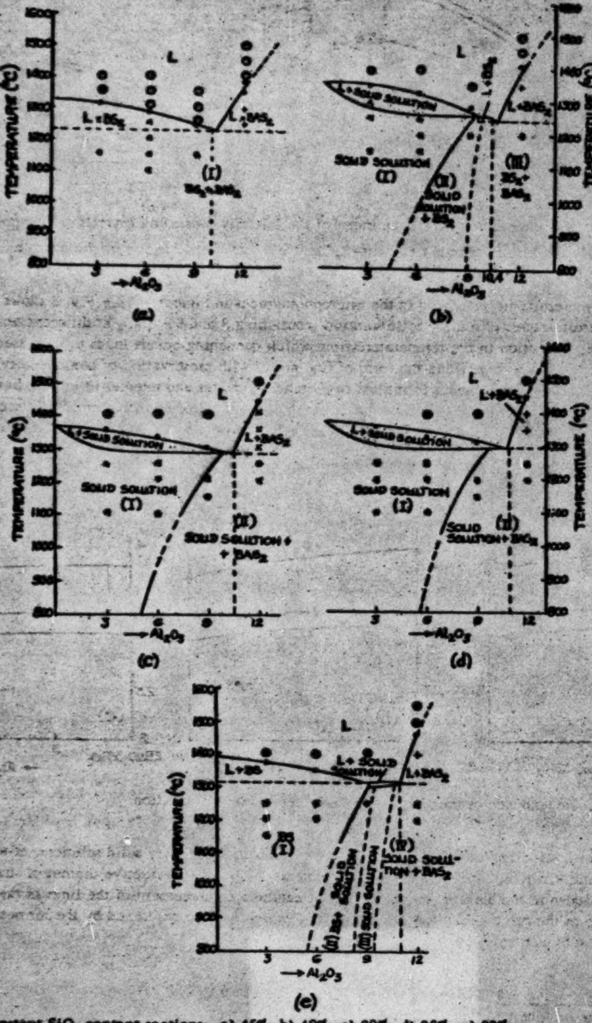


Fig. 14. Constant SiO_2 content sections: a) 45%; b) 42%; c) 39%; d) 36%; e) 33%.

On the basis of the results we have constructed vertical sections parallel to the side $BaO-Al_2O_3$, i.e., sections for constant silica contents of 45, 42, 39, 36 and 33%. The section for 45% SiO_2 [Fig. 14 (a)] passes across the field of barium disilicate and celsian and is a eutectic section. The eutectic corresponds to the simultaneous separation of $BaO \cdot 2SiO_2$ and $BaO \cdot Al_2O_3 \cdot 2SiO_2$ (I). The section for 42% SiO_2 [Fig. 14 (b)] intersects the field of solid solution, barium disilicate, and celsian. The field of existence of solid solution extends within fairly wide limits, and its extent is reduced as the temperature falls (I). A small two-phase region is to be noted; it consists of solid solution and barium disilicate (II). A eutectic is formed between barium disilicate and celsian (III).

The sections for 39 and 36% SiO_2 [Figures 14 (c) and (d)] have much in common: in each case the primary phases are solid solution and celsian. The limits of solid solution are narrowed as the temperature is lowered (I). The eutectic corresponds to the separation of solid solution and celsian (II). The difference between these two sections consists only in the crystallization temperatures of the separate components.

The section for 33% SiO_2 [Fig. 14 (e)] passes across the field of existence of barium metasilicate, solid solution, and celsian. The main field is that of barium metasilicate (I). The field of solid solution occupies a fairly narrow strip (III). Between $BaO \cdot SiO_2$ and the solid solution, a two-phase region exists: this consists of barium metasilicate and solid solution (II). A mixture of the eutectic type is formed between the solid solution and celsian (IV).

SUMMARY

1. It has been established that there is a field of ternary solid solutions formed by barium disilicate, dibarium trisilicate, and celsian, and its boundaries have been defined.

2. The refractive index for this region falls with increase in the contents of barium disilicate and alumina.

3. Five polythermal sections for constant silica contents of 45, 42, 39, 36 and 33% have been constructed; these enable the equilibrium relations to be characterized for the field studied.

Received January 28, 1954

Institute of Silicate Chemistry of the USSR
Academy of Sciences

LITERATURE CITED

[1] P. Eskola, J. Am. Chem. Sci. 4, No. 23, 331 (1922).

[2] R. H. Thomas, J. Am. Ceram. Soc., 33, No. 2, 35 (1950).

ADSORPTION OF VAPOR AT A MERCURY SURFACE

COMMUNICATION 1

B. P. Bering and K. A. Ioileva

The study of the adsorption of gases and vapors at smooth homogeneous solid or liquid surfaces is very important for the elucidation of questions of fundamental significance in the theory of physical adsorption. In these cases the study of adsorption phenomena can be carried out under the cleanest possible conditions, without complications due to the geometric and energetic heterogeneity that is characteristic of the surfaces of technically important sorbents, and without the possibility of capillary condensation in fine pores. Such investigations can considerably extend our concepts of the energetic peculiarities and mechanism of the adsorptionprocess, of the properties of matter in the two-dimensional state, of the phase changes in the adsorption layer, and of the nature of the interaction between the adsorbed molecules. The use of crystalline solids for this purpose cannot completely remove the energetic heterogeneity of the surface, for the adsorption potential depends on the indices of the surfaces of the crystal, on the presence of apexes, edges, and cracks, and also on lattice defects on the surface of the crystal. Also, highly dispersed nonporous crystalline powders are systems having a secondary porosity due to the presence of gaps between the particles in which, at high relative pressures, capillary condensation may occur (at the points of contact of the particles.

On account of these considerations, a liquid mercury surface is of particular interest for the study of the adsorption of the vapors of substances that are insoluble in mercury. In this case, however, direct methods of measuring adsorption are of low accuracy, and much more reliable results can be obtained by an indirect method based on the measurement of the surface tension of mercury in the vapor of the substance concerned, followed by calculation of the amount of adsorption from the Gibbs equation. This method has been applied by a number of authors, but only in the work of Cassel and Salditt [1] and Cassel [2] has the first serious attempt been made to make a systematic study of the adsorption of polar and nonpolar substances on mercury. These investigations enabled the existence of two types of surface-pressure isotherms (and the corresponding adsorption isotherms) to be established. Nonpolar substances give convex surface-pressure isotherms, corresponding to Type I (or II) in Brunauer's classification of adsorption isotherms [3]; surface-pressure isotherms for water and the lower alcohols are concave at low relative pressures and correspond to Type III (or V) adsorption isotherms in the same classification.

Kemball and Rideal [4] and Kemball [5] have recently published a series of investigations in which they have repeated the determinations of Cassel and Salditt by the method based on the measuring of a recumbent drop. As a result of careful experiments, they have shown that all of the substances studied (including water and the lower alcohols) give convex adsorption isotherms, which can be described in the monomolecular region by Volmer's equation. They explain the concave isotherms of Cassel by the presence of contamination, which causes the values found for the surface tension of mercury to be too low.

In 1940, one of the authors of this paper carried out measurements of the surface tension of mercury in water vapor, ethyl alcohol, and butyl alcohol by the method based on the determination of the maximum pressure in drops, and the isotherms obtained for these substances were of Types III and V. Kemball's results conflict markedly with the results of this investigation, and we, therefore, decided to repeat the measurements on the adsorption of a number of substances on mercury by the maximum drop-pressure method. The experimental side of this investigation has been described in detail in our preliminary communication [6].

EXPERIMENTAL RESULTS

The measurement of adsorption by the method under consideration makes very stringent demands with respect to the cleaniness of the mercury surface, and hence, in the judging of the reliability of such measurements, particularly important parts are played by the value of the surface tension of pure mercury and the temperature coefficient of this quantity. The surface tension of mercury was measured in a vacuum in the temperature range 15-96°, and in this range the values obtained can be represented, accurate within ± 0.2%, by the following equation:

$$\sigma_0 = 489.5 - 0.20\ t \qquad (1)$$

The value σ_0 = 484.5 dyne/cm at 25° is in excellent agreement with the value σ_0 = 484.2 ± 0.5 dyne/cm, obtained at the same temperature by Kemball. The value we obtained for $d\sigma_0/dt = -0.20$ agrees exactly with the value obtained by Kemball.

When we had obtained constantly reproducible values of σ_0 we carried out several series of measurements of the surface tension σ in the vapors of water, methanol, acetone, diethyl ether, and heptane at 15, 25, and 40° and at various pressures. In the table we give the values of the surface pressure $\pi = \sigma_0 - \sigma$ and the corresponding values of the relative pressure $h = p/p_0$ for water and methanol. Our experimental results for other substances, and their discussion, will be given in the second communication of this series.

t°	$h \cdot 10^2$	π	$h \cdot 10^2$	π	$h \cdot 10^2$	π	$h \cdot 10^2$	π	$h \cdot 10^2$	π
1	2	3	4	5	6	7	8	9	10	11
Water										
At t = 15° p_0 = 12.79 mm Hg; at t = 25° p_0 = 23.76 mm Hg										
15	38.6	0.0	51.7	1.6	66.5	7.6	81.5	13.7	95.5	21.4
	39.8	0.2	52.6	2.4	68.5	8.6	83.5	14.9	95.5	21.9
	40.0	0.0	54.0	2.7	70.0	9.0	86.0	15.9	98.5	23.7
	44.5	0.5	56.5	3.2	74.0	10.2	86.5	16.8	99.0	23.9
	46.5	0.4	59.5	4.3	75.0	11.0	89.0	17.5	100.0	31.0
	48.4	0.5	62.0	4.1	76.1	12.4	90.5	18.1	100.0	30.8
	49.1	0.8	64.0	6.0	79.5	13.4	91.5	18.5		
	50.5	1.8	64.8	6.6	79.5	12.5	91.5	18.3		
25	30.0	0.1	59.0	3.7	69.5	7.3	82.5	12.8	95.6	22.4
	47.5	0.0	59.0	3.1	71.0	7.3	84.0	12.6	96.5	22.7
	49.0	0.7	60.5	4.1	72.0	8.1	87.6	13.9	98.0	25.6
	52.5	0.6	61.5	5.1	75.0	9.0	89.0	15.3	99.0	27.2
	54.0	2.0	63.0	4.7	77.5	11.2	90.0	16.0		
	56.5	3.2	65.0	6.3	78.6	11.7	94.1	18.8		
	57.0	2.3	66.0	6.3	79.5	12.0	94.5	18.7		
Methanol										
At t = 15° p_0 = 72.0; at t = 25° p'_0 = 123.0; at t = 40° p_0 = 280.0 mm Hg										
15	4.20	0.0	32.7	10.0	59.1	28.4	67.2	34.5	90.4	55.1
	9.70	0.7	41.7	16.3	59.7	29.3	71.0	38.3	90.4	54.9
	12.5	0.9	50.0	21.9	61.2	30.5	71.5	38.1	94.5	61.5
	16.7	1.9	55.6	25.6	62.6	31.6	82.0	47.8	94.5	62.3
	19.5	3.4	56.3	26.1	63.2	31.3	84.0	49.1	100.0	79.1
25	1.10	0.0	10.7	0.7	23.6	4.3	45.0	17.7	78.0	44.1
	2.50	0.0	15.0	1.3	24.8	5.0	49.6	20.2	85.5	50.1
	3.30	0.3	16.3	1.5	31.0	8.1	59.4	27.7	90.5	54.7
	3.90	0.4	18.2	2.1	34.2	10.2	63.5	31.0	98.0	70.0
	9.03	0.5	22.0	3.7	40.7	14.5	66.7	33.8	99.8	81.5
40	1.05	0.0	6.30	0.2	15.1	1.1	21.4	3.0	30.6	7.3
	1.25	0.0	7.60	0.3	16.6	1.2	22.2	3.5	34.7	9.7
	2.32	0.0	10.0	0.5	17.3	1.3	22.8	3.6	38.0	12.0
	4.50	0.0	11.9	0.6	18.0	1.3	25.8	4.8	39.2	12.5
	5.40	0.2	13.2	0.8	19.8	2.3	28.0	5.5	40.9	13.1

In order to calculate the adsorption from the surface-pressure isotherms $\pi = \pi(h)$, the experimental results were expressed in the coordinates (π, log h), and graphical differentiation of the smooth curves drawn through the experimental points yielded values of the adsorption Γ according to the Gibbs equation $\Gamma = (1/kT)(d\pi/d\ln h)_T$ at various values of h. The calculated values of Γ were represented in the coordinates (Γ, log h), and smooth curves were drawn through the points obtained, after which the adsorption isotherms were presented in the usual coordinates (Γ, h).

This method of calculating the adsorption isotherms is very convenient, and it results in a minimum of subjective errors.

In calculations of adsorption from the experimental curves $\pi = \pi(\log \underline{h})$, the question of the accuracy of such calculations arises. It appears that in the general case it is impossible to find the value of the possible error in a derivative when the probable error of discrete values of the function is known. The possibility exists, however, of verifying the correctness of the calculation of the derivative by numerical integration of the derivative function and comparison of the calculated values of the function with the measured values. In our case, in order to check the resulting adsorption isotherms we calculated back from the curves $\Gamma = \Gamma(\log \underline{h})$ in order to obtain the isotherms $\pi = \pi(\log \underline{h})$ (by integration of the Gibbs equation). With this object, by measurement of the area under the curve $\Gamma = \Gamma(\log \underline{h})$ in the interval from $\underline{h}_1$ to $\underline{h}_2$ we determined the value of $\Delta\pi = \underline{k}T \int_{h_1}^{h_2} \Gamma \underline{d} \ln \underline{h}$, the integration being carried out from the lower limit $\underline{h}_1$, corresponding to the maximum measured value π_{max}. The difference $\pi_{max} - \pi$ was represented graphically as a function of $\underline{h}$ and compared with the experimental values of π.

This check, which was carried out for all of the substances studied, gave close agreement between calculated and measured values of π. We give Fig. 1 as an illustration. On this graph the experimental values of π for heptane at 25° are marked by circles, and first of all a smooth curve was drawn through these points. Graphical differentiation of this curve yielded the adsorption isotherm (Curve 2 in Fig. 1). The result of the integration of this curve is represented by the continuous curve 1. As Fig. 1 shows, the experimental points fit very well to Curve 1. This circumstance makes it very probable that the calculated adsorption isotherm corresponds precisely to the experimentally found curve $\pi = \pi(\log \underline{h})$.

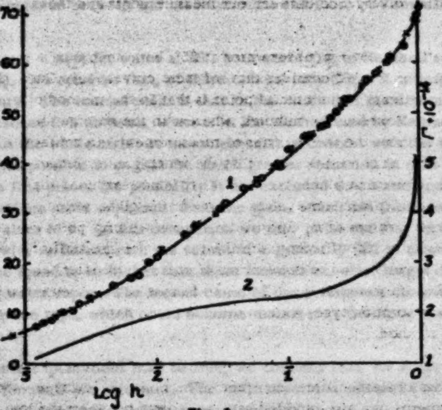


Fig. 1.

Fig. 2 gives the isotherms $\pi = \pi(\log \underline{h})$ for water at 15° (Curve 1) and for methanol at 40° (Curve 2). On the same graph there are shown also the corresponding curves for ethyl alcohol at 20° (Curve 3) and butyl alcohol at 50° (Curve 4), which were obtained previously by one of the authors of this paper. At that time the corresponding measurements for water were not completed, but, in this case also, an appreciable fall in σ in water vapor was observed only for $\underline{h} > 0.5$, and a concave isotherm $\pi = \pi(\underline{h})$ was obtained. It is possible that the lower value of σ_0 found in these experiments (471.0 dyne/cm at 25°) was the result of a systematic error. The values of π for ethyl and butyl alcohols have been increased by 2.7% in Fig. 2, and so adjusted to the value $\sigma_{25^\circ} = 484.5$ dyne/cm.

DISCUSSION OF EXPERIMENTAL RESULTS

It is first necessary to point out the close agreement between the curves $\pi = \pi(\log \underline{h})$ obtained by us and the corresponding curves obtained by Kemball for heptane and acetone. In Fig. 2 the crosses 1 indicate the values of π found by Kemball for heptane at 25°. Equally close agreement is observed also for acetone at 25°. This fact is in

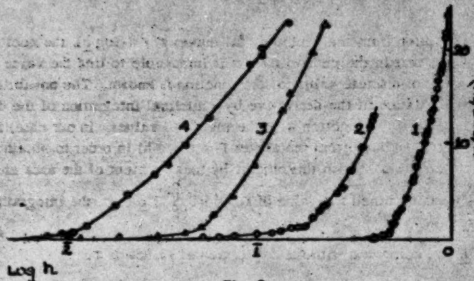


Fig. 2.

itself deserving of attention, since for the first time, in two series of completely independent measurements carried out in different laboratories by different methods, complete agreement has been obtained, not only with respect to the absolute values of σ_0 and $\underline{d\sigma_0/dt}$, but also with respect to the surface-pressure isotherms, and, therefore, the adsorption isotherms of the two substances on mercury. These facts make it all the more surprising that there should be such a notable qualitative divergence between our measurements and those of Kemball in the case of water and alcohols.

In Fig. 3 we give the curves $\pi = \pi(\underline{p})$ for water at 25°, both according to Kemball's results (Curve 1), and also according to our results (Curve 2). We consider that, of these curves, only Curve 2 corresponds to the physical adsorption of water vapor on mercury. The crucial point is that in the method of maximum pressure the time for the formation of the drop does not exceed 2-3 minutes, whereas in the method used by Kemball the mercury surface remains for a long time (throughout the whole series of measurements) in contact with the atmosphere of vapor in the apparatus. It, therefore, seems possible to us that the much greater reduction in σ in Kemball's experiments is due to one of two causes. In the first place, the possibility is not excluded that water and alcohols, being adsorbed on the glass of the apparatus, displace some substances from the glass, which are then adsorbed on the mercury surface and cause increase in the values of π. In this connection we may point out that we have observed that when the apparatus has not been cleaned with sufficient care the values of σ gradually fall at constant water vapor pressure. In this case, the values of π were found to be higher than those found later, after longer evacuation with intermediate "washing" of the apparatus with water vapor. The second cause of the divergence could be the occurrence of slow processes of the activated-adsorption type, which could become manifest in the static method of Kemball, but not in the maximum pressure method.

However, whichever of these explanations may be true, we consider that, for water and alcohols, our measurements are correct, and those of Kemball are incorrect. The main objection advanced by Kemball against the concave surface-pressure isotherms in Cassel and Salditt's paper was based on the low vacuum value of σ_0 (455 dyne/cm at 50°), which Kemball ascribed to the presence of surface-active contamination. It will be clear that this objection cannot be applied to our measurements.

The recently published paper of Karpachev, Smirnov, and Volchenkova [7] has convinced us still more of the incorrectness of Kemball's measurements. In this paper, the authors, without burdening themselves with references to the literature, have described a copy they have made of Kemball's apparatus (in a considerably worsened variant) and have given results of measurements of the surface tension of mercury in a vacuum (σ_0 = 477.4 dyne/cm at 30°) and in water vapor. Curve 3 in Fig. 3 shows their isotherm $\pi = \pi(\underline{p})$ at 30°. Curves 1 and 3 in this figure are far from coincident, although the values of σ_0 are close. In our opinion, this means that neither of these curves has any relation to the physical adsorption of water vapor on the surface of mercury.

Passing to an examination of our results, we will first consider the adsorption isotherms for alcohols and water calculated on the basis of the curves in Fig. 2. Fig. 4 shows the adsorption isotherms for water at 15° (Curve 1), methyl alcohol at 40° (Curve 2), ethyl alcohol at 20°(Curve 3), and butyl alcohol at 50° (Curve 4). For each of these substances, there is a sudden jump in adsorption at constant $\underline{h}$, which is characteristic for a two-dimensional phase transition of the first kind, corresponding to two-dimensional condensation. In this connection we must point out that, as a more careful examination of the results of our measurements has shown, the conclusions reached in our preliminary communication [6] regarding the absence of vertical jumps in the adsorption isotherms is erroneous.

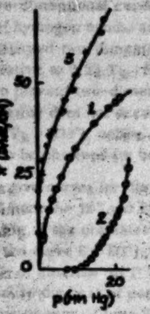


Fig. 3

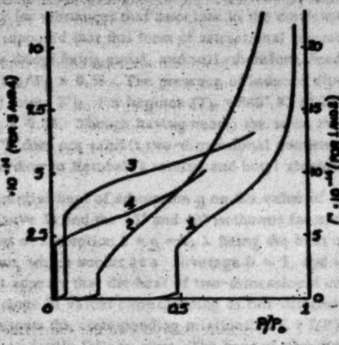


Fig. 4

In 1925 Frumkin showed for the first time [8] that the occurrence of two-dimensional condensation will be indicated by a break in the surface-pressure isotherm. In the work cited such a break was found in the isotherm for the surface pressure of aqueous solutions of lauric acid. On the curves $\pi = \pi(\log h)$ in Fig. 2, distinct breaks can be seen for water and methyl alcohol, the breaks for ethyl and butyl alcohols being less distinct, probably owing to the lower number of experimental points. For the water and methyl alcohol isotherms, the breaks are still present at the other temperatures studied. There is little room for doubt, therefore, that two-dimensional condensation occurs in the physical adsorption of water and lower aliphatic alcohols on mercury in the temperature range 15-40°.

As is well-known, the adsorption isotherms for water and methyl alcohol at graphite and nonporous carbon black surfaces [9] are very similar in form to the isotherm represented by Curve 1 in Fig. 4. It may be considered that this resemblance is due to the identity of the mechanisms in the two cases. The absence of a vertical jump in the adsorption isotherms for water vapor at carbon adsorbents probably arises from surface heterogeneity. Curve 1, Fig. 4, therefore, may be regarded as a confirmation of the correctness of the views on the nature of the adsorption of water vapor on carbon that have been advanced by Dubinin in a number of papers [10].

Comparatively recently phase transitions of the first kind have been found by Harkins and coworkers [11] in the study of the adsorption of heptane on silver, ferric oxide, and graphite. However, careful verification has shown that in the adsorption of heptane on silver [12], and on ferric oxide and graphite [13] no signs of two-dimensional condensation can be detected. It thus appears that only in the work of Clark and Ross [14] has two-dimensional condensation been actually observed (for ethane on sodium chloride). In this connection, the fact that we have established the absence of a first-order phase transition in the adsorption of heptane on mercury may be regarded as further confirmation of the incorrectness of the results of Harkins and coworkers [11].

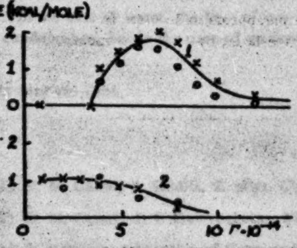


Fig. 5.

On the basis of our results we can make a rough estimate of the value of the two-dimensional pressure π_c at which two-dimensional condensation occurs. The resulting values of π_c for water, methyl alcohol, ethyl alcohol, and butyl alcohol are 0.8, 1.3, 1.0, and 0.8 dyne/cm, respectively. According to Adam [15], for pentadecanoic acid on water π_c = 0.1 dyne/cm, and with reduction in the length of the carbon chain, the pressure π_c rises by approximately 0.1 dyne/cm for each carbon atom removed. If we assume that this relationship is valid also for aliphatic alcohols, then the results of our evaluation of π_c are in accord with these observations.

The accuracy of the measurement of π is insufficient and the temperature range of the measurements is too small to permit the determination of the two-dimensional critical temperature for the substances investigated. As Devonshire [16] has shown from statistical considerations, for the very simple case of the adsorption of the inert gases the ratio of the two-dimensional critical temperature T'_k to the three-dimensional critical temperature is $T'_k/T_k = 0.53$. This ratio, however, depends on the individual properties of the molecules and on their interaction in the adsorption layer. We have observed the phenomenon of two-dimensional condensation on mercury only for substances that associate in the condensed phase under the action of hydrogen bonds, and it may, therefore, be supposed that this form of attractional interaction increases the probability of two-dimensional condensation, other things being equal, and will, therefore, lead to an increase in T'_k relative to 0.53 T_k. For the alcohols studied $T'_k/T_k > 0.53$. The presence of induced dipole moments must tend to prevent two-dimensional condensation and lower T'_k. For heptane (T_k = 540° K) at 15° two-dimensional condensation does not occur, and therefore, $T'_k/T_k < 0.53$. Though having nearly the same critical temperature, acetone (T_k = 508°), unlike ethyl alcohol (T_k = 517°), does not exhibit two-dimensional condensation. A similar picture is to be observed for benzene (T_k = 564°) (according to Kemball's results) and butyl alcohol (T_k = 560°).

In Fig. 5 we give curves for the dependence of the differential heat of adsorption $\underline{q}$ on the value of the adsorption Γ, calculated from the 15° and 25° isotherms for water (Curve 1) and the 25° and 40° isotherms for methyl alcohol (Curve 2). In Fig. 5 the ordinates represent the "pure" heat of adsorption $E = \underline{q} - \lambda$, λ being the heat of condensation. For water the curve $E = E(\Gamma)$ passes through a maximum, which occurs at a coverage $\theta \approx 1$, and which approaches the axis of abscissas as Γ becomes still greater. It appears that the heat of two-dimensional condensation is almost equal to the heat of condensation λ, for in the range of values corresponding to two-dimensional condensation, E is close to zero. Curve 2 in the same figure represents the corresponding relationship $E = E(\Gamma)$ for methyl alcohol. In this case, E has no distinct maximum and gradually falls to zero. The heat of two-dimensional condensation exceeds λ by about 1 kcal/mole.

The calculation of E for water and methyl alcohol was carried out in the first place by the Clausius-Clapeyron equation $E = RT^2(\underline{d}\ln\underline{h}/\underline{d}T)_\Gamma$, and in the second place by the Williams equation [17]:

$$E = \frac{d}{d\Gamma}\left[\pi - T\left(\frac{d\pi}{dT}\right)_h\right] \qquad (2)$$

directly from two $\pi = \pi(\log \underline{h})$ isotherms corresponding to two different temperatures. The results of the calculation by the first method are denoted in Fig. 5 by crosses, and those obtained by the second method, by circles. The difference in the calculated values of E gives an idea of the possible calculation error.

The authors are greatly indebted to V. V. Serpinsky, M. M. Dubinin, and B. V. Ilyin for their interest in the work and valuable advice.

SUMMARY

1. By a method based on the maximum pressure in a drop, measurements have been made of the surface tension of mercury in a vacuum, in water vapor, and in methanol vapor. In the temperature range 15-96° the surface tension of mercury is expressed by the formula $\sigma = 489.5 - 0.20\,\underline{t}$.

2. On the basis of these measurements, adsorption isotherms have been calculated for the vapors of these substances on mercury. The previously obtained adsorption isotherms for ethyl and butyl alcohols are also given.

3. In the adsorption of water and alcohols on mercury, a first-order two-dimensional phase transition has been observed, corresponding to two-dimensional condensation. It has been shown that the results of analogous measurements by Kemball for water and alcohols are incorrect.

4. In the case of water, the heat of two-dimensional condensation appears to be close in value to the usual heat of condensation, but in the case of methanol the former exceeds the latter by 1 kcal per mole.

Received May 26, 1954

Institute of Physical Chemistry of the
USSR Academy of Sciences

LITERATURE CITED

[1] H. M. Cassel, F. Salditt, Z. phys. Chem., 155A, 321 (1931).

[2] H. M. Cassel, Z. f. Elektrochem., 37, 642 (1931); Trans. Faraday Soc., 28, 177 (1932).

[3] S. Brunauer, Adsorption of Gases and Vapors, Vol. I, Foreign Lit. Press, Moscow, 1948.

[4] C. Kemball, E. K. Ridel, Proc. Roy. Soc., 187 A, 53 (1946).

[5] C. Kemball, Proc. Roy. Soc., 187 A, 73 (1946); 190 A, 117 (1947); 201 A, 377 (1950).

[6] B. P. Bering and K. A. Ioileva, Proc. Acad. Sci. USSR, 93, 85 (1953).

[7] S. V. Karpachev, M. V. Smirnov, and Z. S. Volchenkova, J. Phys. Chem., 27, 1228 (1953). *

[8] A. N. Frumkin, Z. phys. Chem., 116, 466 (1925).

[9] C. Pirce, R. N. Smith, J. Willy, H. Cordes, J. Am. Chem. Soc., 73, 4551 (1951); C. Pirce, R. N. Smith, J. Phys. Colloid. Chem., 54, 354 (1950).

[10] M. M. Dubinin and E. D. Zaverina, J. Phys. Chem., 21, 1373 (1947).

[11] G. Jura, E. H. Loeser, W. D. Harkins, P. R. Basford, J. chem. Phys., 13, 535 (1945); J. Am. Chem. Soc., 68, 554 (1946); J. Chem. Phys., 14, 117, 344 (1946).

[12] D. M. Joung, R. A. Beebe, H. Bienes, Trans. Faraday Soc., 49, 1086 (1953).

[13] R. N. Smith, J. Am. Chem. Soc., 74, 3477 (1952).

[14] H. Clark, S. Ross, J. Am. Chem. Soc., 75, 6081 (1953).

[15] N. K. Adam, Physics and Chemistry of Surfaces, State Tech. Press, Moscow, 1948.

[16] A. Devonshire, Proc. Roy. Soc., 163 A, 132 (1947).

[17] A. M. Williams, Proc. Roy. Soc., (Edinburgh).38, 23 (1918).

---

* Complete translation of the referenced article is available from Consultants Bureau. Price, $15.00.

SYSTEMS CONTAINING HYDROGEN PEROXIDE AT HIGH CONCENTRATION

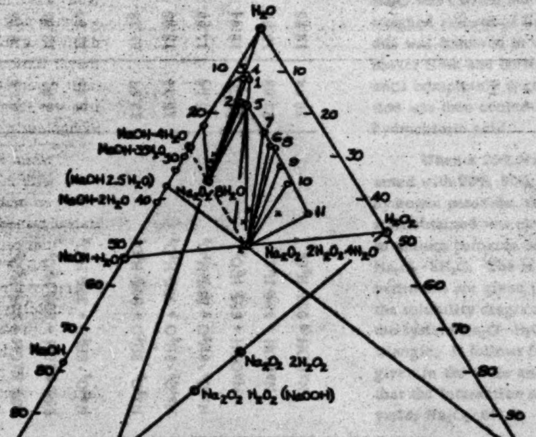
COMMUNICATION 7. 0° ISOTHERM OF THE TERNARY SYSTEM $NaOH-H_2O_2-H_2O$

S. Z. Makarov and N. K. Grigoryeva

The investigation of the ternary system $NaOH-H_2O_2-H_2O$ by the solubility method was undertaken in connection with the study of a number of questions relating to the interaction of hydrogen peroxide solutions and the hydroxides of alkali and alkaline-earth metals. These reactions, as our investigations have shown, are accompanied not only by the formation of hydrated forms of the peroxide compounds of the metals, but also, at higher hydrogen peroxide concentrations, by the formation of perhydrates – products of the addition of H_2O_2, and possibly compounds of the so-called hydroperoxide type. It should be noted that a completely clear picture of the nature of these substances is not yet to be found in the literature, and for this reason the most diverse ideas are to be found concerning the structure of the so-called hydroperoxides, in spite of the large number of investigations that were made in the period 1862-1912.

Of these investigations, the most significant are those of Harcourt [1], Schöne [2], Tafel [3], D'Ans and Friedrich [4], Wolffenstein and Peltner [5], and Pisarzhevsky [6]. For the hydroperoxide compounds of sodium the following forms have been indicated: 1. NaOOH or $Na_2O_2 \cdot H_2O_2$; 2. $NaOOH \cdot 0.5H_2O_2$ or $Na_2O_2 \cdot 2H_2O_2$; 3. $NaOOH \cdot 0.5H_2O_2 \cdot 2H_2O$ or $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$. The sodium peroxide hydrates indicated were: 1. $Na_2O_2 \cdot 8H_2O$, the octahydrate; 2. $Na_2O_2 \cdot 2H_2O$, the dihydrate; 3. $Na_2O_2 \cdot H_2O$, the monohydrate.

If we start from the simplest concepts concerning normal peroxide compounds as products of the replacement of hydrogen in the H_2O_2 molecule by metal, we can obviously have only two kinds of compounds: M–OOH and M–O–O–M, i.e., M_2O_2 – the so-called hydroperoxides and peroxides. These compounds may become more complicated by the addition of molecules of H_2O and H_2O_2. It will be clear that for the final solution of the question of the actual structures of these compounds, special investigations directed to the determination of these structures must be carried out.



TABLE

Data Relating to 0° Isotherms

Point No.	Composition of original medium	Composition of the liquid phase (% by wt.)				Composition of residue (% by wt.)				Solid phase
		active O_2	Na_2O	H_2O	$\frac{O_2}{Na_2O}$	active O_2	Na_2O	H_2O	$\frac{O_2}{Na_2O}$	
3	25% NaOH + 56% H_2O_2	2,84	9,18	87,98	0,309	6,31	26,21	67,48	0,240	$Na_2O_2 \cdot 8H_2O$
4	25% NaOH + 72% H_2O_2	2,88	8,30	88,82	0,347	5,94	25,06	69,00	0,235	The same
1	25% NaOH + 20% H_2O_2	3,14	8,78	88,06	0,357	5,59	23,31	71,10	0,239	"
2	25% NaOH + 30% H_2O_2	4,81	12,41	82,78	0,387	6,11	21,61	72,28	0,281	"
5	$Na_2O_2 \cdot 8H_2O$ + 30% H_2O_2	6,45	11,54	82,01	0,553	14,64	23,85	61,51	0,613	$Na_2O_2 \cdot 8H_2O$ + + $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$
7	$Na_2O_2 \cdot 8H_2O$ + 80% H_2O_2	12,67	11,28	76,05	1,123	18,78	26,57	54,65	0,706	$Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$
6	$Na_2O_2 \cdot 8H_2O$ + 72% H_2O_2	15,31	12,28	72,41	1,246	18,85	23,78	57,37	0,792	The same
8	$Na_2O_2 \cdot 8H_2O$ + 88% H_2O_2	16,24	11,33	72,43	1,430	20,32	23,33	56,35	0,874	"
9	NaOOH + 65% H_2O_2	19,75	12,44	67,81	1,580	20,30	25,20	54,50	0,805	"
10	NaOOH + 88% H_2O_2	22,62	13,66	63,72	1,650	21,17	30,39	48,44	0,696	"
11	NaOOH + 93% H_2O_2	30,74	12,90	56,36	–	24,61	18,30	57,09	–	"

EXPERIMENTAL

At first it was proposed to study isotherms for above 0°, but it was found that under these conditions rapid decomposition reactions occur, so that it is more expedient to study isotherms for the system $NaOH-H_2O_2-H_2O$ at low temperatures. The investigation of the 0° isotherm was carried out in a thermostat in which the constant temperature was maintained by means of ice or snow.

The initial reactants were NaOH solutions of various concentrations and hydrogen peroxide solutions, free from stabilizers, and again of various concentrations. It was established by preliminary experiments that it was not desirable to use very strong NaOH solutions, since the reaction between NaOH and H_2O_2 yielded much heat and resulted in large losses of oxygen. The most suitable NaOH concentration was found to be about 25-30%.

Active oxygen was determined by a permanganate method, as follows: a sample of the liquid phase or residue was transferred to a weighed beaker containing boric acid, and the sample was dissolved in cooled water and titrated with potassium permanganate in presence of sulfuric acid. The determination of Na_2O was carried out as follows: the weighed amount of liquid phase or residue was dissolved in water in an Erlenmeyer flask and boiled for 1-2 hours until completely decomposed; the solution was then cooled and titrated with hydrochloric acid.

When a 25% NaOH solution interacted with 20%, 30%, 56%, and 72% hydrogen peroxide, the residue of crystals obtained was close in composition to sodium peroxide octahydrate $Na_2O_2 \cdot 8H_2O$. The results of these experiments are given in the table and in the solubility diagram, which represents the system $Na_2O-H_2O-0.5O_2$ on a Gibbs triangle. It follows from the results given in the table and in the diagram that the interaction of NaOH and H_2O_2 yields $Na_2O_2 \cdot 8H_2O$.

When crystals of $Na_2O_2 \cdot 8H_2O$ reacted with 30%, 72%, 80% and 88% hydrogen peroxide at 0°, a compound was obtained that was close in composition to the so-called "hydroperoxide" $NaOOH \cdot 0.5H_2O_2 \cdot 2H_2O$ (or $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$). In spite of further increase in the concentration of H_2O_2 in the liquid phase at this temperature, no compounds richer in oxygen were obtained.

When the crystals obtained as above were immediately treated with a new portion of 65% or 88% H_2O_2, only the original phases were obtained. When the crystals of "sodium hydroperoxide" were treated with 93% hydrogen peroxide, a residue was obtained that rapidly began to decompose. The solubility diagram that we obtained for the 0° isotherm consists of two clearly defined branches corresponding to saturation with respect to the two solid phases $Na_2O_2 \cdot 8H_2O$, and $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$. The $NaOH \cdot 4H_2O$ branch is extremely small; the initial solubility of NaOH is 29.2%, the solid phase being $NaOH \cdot 4H_2O$. The limits of the existence of $Na_2O_2 \cdot 8H_2O$ are determined by the composition at the multiple point (No. 5 in the table). The limiting concentration attained by H_2O_2 in the liquid phase at 0° is about 65%, and the solid phases are then insufficiently stable and the residues readily decompose.

SUMMARY

1. The 0° isotherm of the system $NaOH-H_2O_2-H_2O$ has been studied for H_2O_2 contents of up to 65% in the liquid phase by the solubility method.

2. The presence of three solid phases has been established, their compositions being $NaOH \cdot 4H_2O$, $Na_2O_2 \cdot 8H_2O$, and $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$. The last phase, $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$, can be regarded also as a hydroperoxide of composition $NaOOH \cdot 0.5H_2O_2 \cdot 2H_2O$, but special investigation will be necessary to determine which is the actual form.

3. Sodium peroxide octahydrate $Na_2O_2 \cdot 8H_2O$ has been prepared in well-formed, platelike crystals, which are quite stable when kept in the cold. They are converted by dehydration into anhydrous sodium peroxide.

Received April 27, 1954

N. S. Kurnakov Institute of General and Inorganic
Chemistry of the USSR Academy of Sciences

LITERATURE CITED

[1] V. Harcourt, Quart. J. Chem. Soc., 14, 267 (1862).

[2] E. Schöne, Ann., 193, 241 (1878).

[3] J. Tafel, Ber., 27, 2297 (1894).

[4] J. D'Ans and W. Friedrich, Z. anorg. Chem., 73, 327 (1912).

[5] R. Wolffenstein and E. Peltner, Ber., 41, 281 (1908).

[6] L. V. Pisarzhevsky, Peroxides and Peracids, Odessa, 1902.

BABINET'S PRINCIPLE, AND THE LOW-ANGLE SCATTERING OF X-RAYS BY POROUS GLASSES

E. A. Porai-Koshits and V. N. Filipovich

The application of the method of low-angle X-ray scattering to the study of the structure of highly dispersed porous substances (gels, catalysts, porous glasses, etc.) meets with a number of specific difficulties associated not only with the variety of dimensions, form, and spatial distribution of the dispersed substance, but also with the applicability of the so-called Babinet's principle. Some authors, in determining the radii of the heterogeneous regions by this method, have associated them with the dimensions of the particles [1], whereas others have associated them with the dimensions of the pores [2]. In many cases, the problem of "pores or particles" has been solved by comparison of X-ray data with data obtained by other methods (electron microscope studies, sorption measurements, etc.), but owing to the relatively recent development of all these methods of studying the submicroscopic structure of materials full concurrence of results has been attained only in the simplest cases; generally, however, it has been shown that there is an absence of conflict between results obtained by different methods, but this, of course, is not a direct and unequivocal proof of a solution to this problem.

In the first part of this paper we examine the essential nature of Babinet's principle and its applicability to the scattering of X-rays at low angles. In the second part, we give the results of a special investigation directed to the solution of the problem of "pores or particles" for the case of porous glasses (preliminary studies of the structure of these glasses by the low-angle method have been described previously [3]).

1.

As is well-known [4], the intensity $I(\vec{s})$ of X-rays scattered by a specimen of volume V in the direction of the unit vector $\vec{s}_1$, may be expressed (under the conditions for Fraunhofer diffraction) in the following form:

$$I(\vec{s}) = \frac{I_0}{D^2}\left(\frac{e^2}{mc^2}\right)\frac{1+\cos^2 2\theta}{2}\left|\int_V \rho(\vec{r})e^{i(\vec{s}\,\vec{r})}dV\right|^2; \tag{1}$$

(D is the distance from the specimen to the film; $\vec{s} = \frac{2\pi}{\lambda}(\vec{s}_1 - \vec{s}_0)$, in which λ is the wavelength; $\vec{s}_0$ is the unit vector in the direction of the incident parallel beam; $\theta = \frac{\vec{s}_1\vec{s}_0}{2}$, half of the scattering angle; and $\rho(\vec{r})$ is the electron density of the specimen). Dividing Equation 1 by the preintegral factor and keeping the same expression on the left hand side ($I(\vec{s})$), we have:

$$I(\vec{s}) = \left|\int_V \rho(\vec{r})\,e^{i(\vec{s}\,\vec{r})}\,dV\right|^2. \tag{2}$$

The solution of this equation with respect to $\rho(\vec{r})$ forms the main problem of X-ray structure analysis.

Apart from purely mathematical difficulties in the satisfactory solution of Equation 2 (these depend on the nature of the scattering object, which may be a gas, crystal, liquid, or amorphous solid), there is one question of principle that makes the unequivocal determination of $\rho(\vec{r})$ from $I(\vec{s})$ practically impossible. The essential point is that generally $I(\vec{s})$ can be determined experimentally with sufficient accuracy only for scattering angles exceeding a certain small angle, the value of which depends on the setting and accuracy of adjustment of the apparatus; and in this connection particular importance must be attached to Babinet's principle, the essential nature of which will be clear from the following.

Let us express $\rho(\vec{r})$ in the form:

$$\rho(\vec{r}) = \overline{\rho(\vec{r})} + \Delta\rho(\vec{r}). \tag{3}$$

in which $\overline{\rho}(\vec{r})$ is the average electron density within the specimen:

$$\overline{\rho}(\vec{r}) = \frac{1}{V} \int \rho(\vec{r})\, dV$$

and is zero outside the specimen; $\Delta\rho(\vec{r})$ is the departure of the value of the electron density from the value $\overline{\rho}$.

From Equations 2 and 3 we obtain:

$$I(s) = \left| \int [\overline{\rho}(\vec{r}) + \Delta\rho(\vec{r})]\, e^{-i(\vec{s}\,\vec{r})}\, dV \right|^2 = \left| \int \overline{\rho}(\vec{r}) e^{i(\vec{s}\,\vec{r})}\, dV \right|^2 + 2\mathrm{Re} \int \overline{\rho}(\vec{r}_1) e^{i(\vec{s}\,\vec{r}_1)}\, dV_1 \int \Delta\rho^*(\vec{r}_2) e^{-i(\vec{s}\,\vec{r}_2)}\, dV_2 + \left| \int \Delta\rho(\vec{r}) e^{i(\vec{s}\,\vec{r})}\, dV \right|^2. \tag{4}$$

The first two terms in Equation 4 determine the so-called "zero-angle scattering"; they both contain, as a factor, the integral

$$\int \overline{\rho}(\vec{r}) e^{i(\vec{s}\,\vec{r})}\, dV, \tag{5}$$

corresponding to the amplitude of the scattering of an ideally homogeneous specimen, and therefore, differing from zero only for $s < s_0$, s_0 being a very small quantity; i.e., at very low scattering angles. We may point out that the evaluation of the value of s_0 so that for $s > s_0$ the zero-angle scattering can be neglected cannot be based on the Fraunhofer approximation for the usual experimental arrangement: the treatment must be based on Fresnel diffraction. Such an evaluation, however, is associated with further mathematical difficulties, and we shall not carry it out. The evaluation that we have given previously for scattering by a liquid [5] did not take this circumstance into account. As experiment shows, the values of s_0 are in any case very much lower than the values of s at which low-angle scattering is to be observed, even when the dimensions of the scattering particles are very great (of the order of 1000 A). This is evidenced by the existence of comparatively homogeneous materials (and they are in a majority) that do not give low-angle scattering even when exposures of hundreds of hours are given; although, of course, they show zero-angle scattering.

Let us examine now the intensity of the scattering $I'(\vec{s})$ by a specimen having an electron density $\rho'(\vec{r})$ such that

$$\rho'(\vec{r}) = \rho_0(\vec{r}) - \rho(\vec{r}) = \rho_0(\vec{r}) - \overline{\rho}(\vec{r}) - \Delta\rho(\vec{r}) = \overline{\rho}'(\vec{r}) - \Delta\rho(\vec{r}); \tag{6}$$

(in this equation $\rho_0(\vec{r})$ may be considered, within wide limits, to be an arbitrary constant inside the specimen, and equal to zero outside the specimen). It is obvious that, if we do not wish $\rho'(\vec{r})$ to have negative values, it is necessary that $\rho_0(\vec{r})$ within the specimen should not be less than the maximum value of $\rho(\vec{r})$. The value of $\rho'(\vec{r})$ is a maximum when that of $\rho(\vec{r})$ is a minimum (and vice versa), and therefore characterizes a structure that is complementary or reversed with respect to the structure $\rho(\vec{r})$.

It will be clear that, if we neglect the difference in the absorption coefficients for the structures having electron densities $\rho(\vec{r})$ and $\rho'(\vec{r})$, then the difference between $I(\vec{s})$ and $I'(\vec{s})$ will consist only in the terms corresponding to zero-angle scattering (see the first two terms in Equation 4). If we neglect these terms, which can be done for $s > s_0$, then both intensities are the same, i.e., the scattering intensity is the same for the "direct" structure as for the "reverse" structure (in the sense of Equation 6), and this forms the essence of Babinet's principle. On the basis of the diffraction pattern, therefore, it is impossible to make a choice between the two structures, and for the solution of this question it is necessary to make use of other data.

2. EXPERIMENTAL

In order to solve the problem of "pores or particles" for porous glasses by the use of the low-angle scattering method, the glasses were treated with alkali and with hydrofluoric acid in order to widen the pores artificially. It would be expected that such widening would be accompanied by change in the form of the scattering curve (dependence of intensity on angle), and the direction of this change — to lower or to higher scattering angles — should show whether it is increase in the dimensions of pores or reduction in the thickness of walls that is finding expression.

The first object selected for study was a highly dispersed porous glass prepared from a sodium borosilicate glass containing (in mole-%) 5 of Na_2O, 20 of B_2O_3, and 75 of SiO_2; the low-angle diffraction pattern produced by this glass was sufficiently extensive to permit convenient observation of any changes. A specimen of the original porous glass in the form of a fairly coarse-grained powder (40-70 mesh) was treated with 0.5 N KOH for two hours (this specimen will be indicated by the symbol KOH-2), washed in running water until the phenolphthalein reaction for alkali was negative, and dried. A second treatment in alkali under the same conditions for a further two hours was then carried out. The same procedure was repeated many times, but in certain cases the duration of the alkaline treatment was limited to one hour. Washing with water after each one- or two-hour treatment with alkali was carried out in order to effect uniform removal of products of the breakdown of the glass; and washing in running* water prevented the formation of secondary silicic acid by the hydrolysis of silicates and its coagulation in the pores of the glass. We must point out that in the course of this treatment —after the repeated action of alkali (ten hours)— the outward appearance of the powder began to change: whereas at first the flowing water carried away the finest particles of porous glass and the average size of the residual particles was reduced inappreciably by the action of the alkali, after a ten-hour treatment the powder began to change from the granular form into dust; after a fourteen-hour treatment a suspension of the powder in water was like a colloidal solution, and settled extremely slowly.

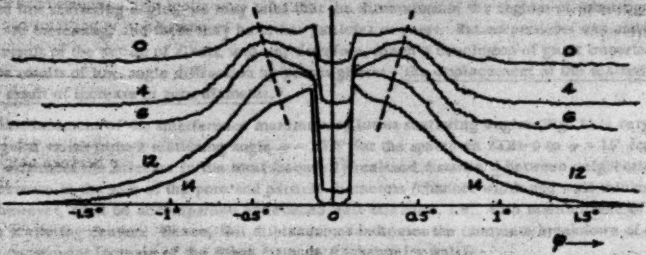


Fig. 2. Microphotometric curves of specimens of highly dispersed porous glass. The numbers indicate the total number of hours for which the glasses were treated with alkali.

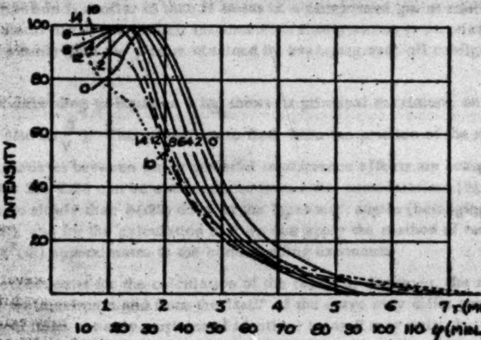


Fig. 3. Intensity curves of highly dispersed porous glass after alkali treatments of varying duration (total number of hours of treatment indicated by numbers).

The X-ray analysis was carried out with CrK_α radiation ($\lambda = 2.29$ A), which was rendered monochromatic by reflection at a monocrystal of calcite in the apparatus previously described [3]. Fig. 1 [see plate, page 171] shows two X-ray pictures: one of the original specimen KOH-0, and the other of the specimen KOH-4, i.e., the specimen given two two-hour treatments in alkali. It will be readily seen that scattering due to the first specimen extends at least 1 mm further than that of the second specimen. Microphotometric measurements and the intensity curves derived from the photographic blackening gave convincing confirmation of this result (Figures 2 and 3).

---

* (Rather than in stationary).

As we were interested above all in the change in the form of the scattering curve as an expression of change in the geometry of the scattering body, we have given the intensity curves of all of the specimens investigated in Fig. 3, in which the height of the interference maximum is taken in each case to be one hundred arbitrary units of intensity. These curves clearly illustrate the regular change in the structure of the porous glass during its treatment with alkali, i.e., during the artificial enlargement of the pores. Since this is accompanied by a regular displacement of the curves toward low scattering angles, we may infer that the dimensions of the regions of inhomogeneity effecting the scattering are increasing, and these may be either particles or pores. But no particles can undergo increase in dimensions as a result of the action of alkali, and we, therefore, reach a conclusion of great importance for the interpretation of the results of low-angle diffraction by porous glasses: the displacement of the scattering curves to smaller angles is a result of increase in pore diameter.*

The regular displacement of the interference maximum to lower scattering angles (Fig. 3) is very marked: its position on the diagram varies from a scattering angle $\varphi = 29.5'$ for the specimen KOH-0 to $\varphi = 19'$ for KOH-10. This displacement evidences the increase in the most frequently realized distance d between neighboring scattering centers, i.e., the increase in the sum of the pore and particle diameters (channel width and wall thickness). Increase in channel width, however, must be accompanied by reduced wall thickness, i.e., with maintenance of a constant distance d between scattering centers. Hence, this displacement indicates the complete breakdown of some of the thinnest walls with consequent increase of the mean distance d (channel + wall).

This interpretation is confirmed by calculations of the radii of the regions of inhomogeneity made after introduction of the collimation correction associated with the use of narrow slits instead of pin-hole diaphragms [7].

Our calculations were based on the relationship

$$I(s) = N\rho^2 v^2 \Phi^2(sR)\left[1 - \frac{\Omega}{V}\Phi(s2R)\right]; \tag{7}$$

(N is the number of regions of inhomogeneity (particles or pores); $\rho = \rho_a - \rho_b$, in which ρ_a is the average electron density of the particles, and ρ_b is the electron density of the medium filling the spaces between the particles (the pores); $\underline{v}$ is the volume of a single region of inhomogeneity; $\Omega = \frac{4}{3}\pi(2R)^3 N$). Equation 7 can be obtained from Equation 2 (see [4] and [7]), on the assumption that 1) the regions of inhomogeneity have, on the average, the form of identical spheres; 2) their distribution is similar to that of atoms in a compressed gas at equilibrium; and 3) the general picture of scattering from atoms of the gas in their instantaneous configuration is practically indistinguishable (for a sufficiently large number of atoms) from the picture obtained by averaging over all configurations for an arbitrary interval of time.

It may be shown [8] that according to Equation 7 $I(\underline{s})$ shows its principal maximum, on the average, at $sR = 2.0-2.25$ (its position depends also on $\frac{\Omega}{V}$). This permits us to find, from the position of the maximum, an approximate value of the radius R of particles between which powerful interference effects are being produced. We may note that the condition that $sR = 2.0-2.25$ can be obtained also from other considerations [9]. On the other hand, since $\Phi(sR)$ falls with angle more slowly than $\Phi(s2R)$ does, at the "greatest" angles (belonging, of course, to the low-angle region) $I(s) \approx N\rho^2\underline{v}^2\Phi^2(sR)$, and for the calculation of R we can apply the method of tangents [7, 8] to the "tail" of the curve and assume that $\Phi^2(sR)$ approximates to the corresponding exponents.

Hence, two different methods exist for the calculation of the radius R. However, the results of the determinations of R from the position of the maximum and from the "tail" of the curve may differ greatly from one another in many cases, for in an actual specimen not only particles of identical mean R may exist, but also particles of other dimensions R_i, which, forming, for example, a semblance of a rarified gas ($\Omega \ll V$), will give scattering of the form

$$I(s) = \rho^2 \sum_i N_i v_i^2 \Phi^2(sR_i) \tag{8}$$

(we assume that $\rho_i = \rho$). This scattering, while only slightly distorting the position of the interference maximum, may greatly affect the scattering picture at the "greatest" angles (i.e., in the region of the "tail" of the curve) in the case of low values of R_1, or at the "least" angles in the case of high values of R_1. We may note also that in Equations 7 and 8 Babinet's principle is expressed by the fact that $I(s)$ depends only on the square of the difference $\rho_a - \rho_b$, so that change in the sign of this difference (i.e., transition from the "direct" to the "reverse" structure) has no effect on $I(\vec{s})$.

---

* It is of interest to recall an analogous result obtained recently by Guinier [6] for the thermal treatment of an alloy of silver and aluminum. In both cases, the displacement of the maximum to lower angles is interpreted as increase in the radii of regions of inhomogeneity. In correspondence with its dependence on the treatment of the objects investigated, Guinier associated this increase with increase in the size of crystal clusters rich in silver, and we—with increase in pore size. The identical diffraction effect in the two cases is an excellent illustration of the applicability of Babinet's principle to the low-angle scattering of X-rays.

In our calculations, we applied both of these methods. Since the exact determination of the absolute values of pore radii (which depend also on the thermal history of the original glass) was not involved in our problem, our concern being only with their relative changes in the course of alkaline treatments, the collimation correction was made by a highly simplified method [6]. Nevertheless, as can be seen from Table 1, the two methods of calculating the

TABLE 1

Calculation of Pore Radii of Finely Porous Glass

X-Ray Photograph No.	Duration of alkaline treatment (hours)	Pore radius according to position of maximum (A)	Pore radius according to "tail" of curve				
			R_1 (A)	content (% by volume)	R_2 (A)	content (% by volume)	R_{av} (A)
527 634 1052	0	64	50	70	107	21	62
1057	2	69	62	75	103	25	72
546 1033	4	77	65	70	110	30	77
1043	6	85	72	68	115	32	86
547 1047	8	92	68	62	121	38	88
1035	10	96	47	30	130	70	104
1034	12	100	42	50	100	50	71
1042	14	–	33	70	72	30	45

radii gave agreeing results for all of the specimens, from KOH-0 to KOH-10, and these indicated gradual enlargement of the pores. When the action of the alkali was prolonged (ten hours or more) —as can be seen not only from Table 1, but also from Figures 2 and 3— the variation in the form of the scattering curves takes on a rather different character: extra scattering at the "greatest" angles appears, and the sharpness of the interference maximum is somewhat reduced. This may be explained by incipient destruction of the porous grains of the glass, which results in additional scattering by highly dispersed nonporous particles (radii 47, 42, and 33 A) and in reduction in the intensity of the main scattering by porous grains accompanied by a general increase in the total intensity. This interpretation is confirmed by the increase that occurs in the content by volume of particles of the lowest radii as the action of alkali proceeds, and also by a comparison of the outward appearance of grains of the specimen KOH-6 and KOH-14 under the microscope (magnification 720): whereas in the first case particles of glass of characteristic fracture were clearly visible, in the second case these were replaced by fine formations having uneven edges and rough surfaces. We should point out that the calculation of the second radius for the first five specimens is not completely valid; nor is the calculation of average radii for these samples (Column 8). However, the very close agreement of these values with the values calculated from the position of the maximum justifies this calculation. The calculation of the second radius from the "tails" of curves for specimens treated with alkali for more than ten hours (the last three specimens in Table 1) is of greater validity, since the effect of the interference maximum is here negligible. The fact that this radius is systematically greater than that calculated from the position of the maximum is to be expected: in subtracting the scattering due to particles having the first radius (in this case, nonporous particles) from the general scattering curve, we are bound to include part of the scattering due to the finest pores of intact grains in

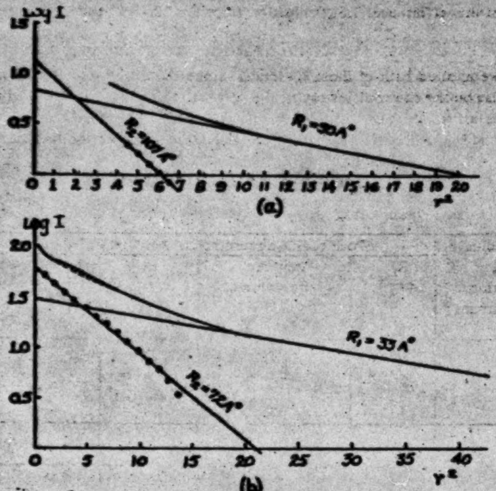


Fig. 4. Graphical calculation of pore radii for a highly dispersed specimen of porous glass: a) before treatment with alkali; b) after a fourteen-hour treatment with alkali.

the subtracted intensity, so that a high value will be obtained for the second radius. In Fig 4 we give two curves illustrating the graphical calculation of the radius from the "tail" of the curve (r is the distance from the center of the primary beam (mm), and is proportional to the scattering angle).

The glass investigated was one of the most highly dispersed, and conclusions arrived at on the basis of its study cannot be extended to more coarsely grained and more coarsely porous specimens without verification. Hence, as a second object for investigation in an analogous way, a specimen having coarser grains and larger pores was taken; it

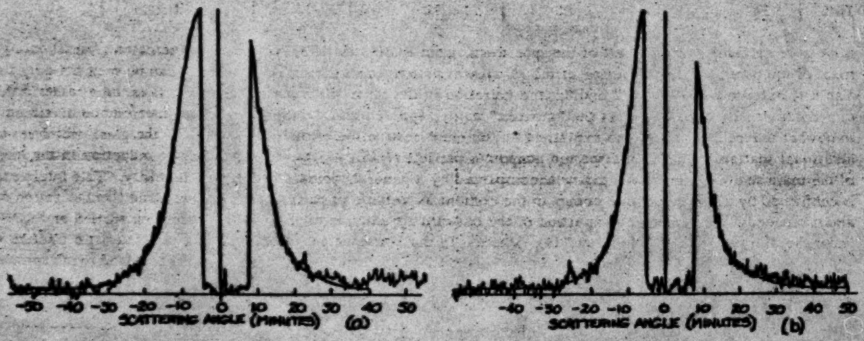


Fig. 5. Microphotometric curves for a coarsely porous glass: a) treated with alkali for eight hours; b) treated further with hydrofluoric acid.

was obtained from a sodium borosilicate glass containing 7% of Na_2O, 23% of B_2O_3, and 70% of SiO_2. Since this sample was much less subject to attack by 0.5 N KOH, it was treated with alkali for eight hours (with washes after every two hours) and with an 8% solution of hydrofluoric acid for 15 minutes. So that the dissolution of the silica skeleton should proceed sufficiently vigorously, not only outside but also inside, the porous glass powder was first placed in a thin-walled glass tube, which was heated to 250-300° and evacuated to a high vacuum; it was then immersed in the hydrofluoric acid and broken, thus ensuring that all of the pores of the specimen were rapidly filled with acid.

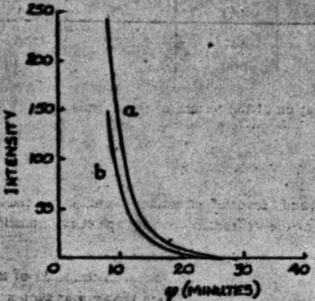


Fig. 6. Intensity curves for coarsely porous glass: a) untreated; b) treated with hydrofluoric acid.

Figures 5 and 6 show the microphotometric and intensity curves for the specimen before and after treatment with hydrofluoric acid (CrK_{α} radiation; $\lambda = 2.29$ A). They indicate the appreciable enlargement of pores that results from this treatment: the scattering curve for the specimen not treated with hydrofluoric acid (a) falls to zero more slowly than the curve for the treated specimen (b). Calculations made by the method of tangents (Fig. 7) enabled us to obtain three values of "coarse" radii in each case. From the intercepts made by the tangents on the axis of ordinates the relative contents by volume of the pores of each radius were calculated, and the mean radii were also calculated, and were found to be 360 and 400 A, respectively, (Table 2).

The distribution of radii according to size indicates the possible presence of yet larger pores in each sample; the scattering due to these is caught by the trap for the primary beam, the trace of which can be seen in Fig. 1 [see plate, page 171] as a light band in the center (the lowest possible scattering angle was 6.5 minutes of arc). There is no doubt, however, about the increase of the average radius in the region observed; and this confirms the general conclusion of the present investigation, which has removed the difficulty arising in the interpretation of X-ray diagrams owing to the applicability of Babinet's principle to the low-angle scattering of X-rays and has solved the "pores or particles" problem for porous glasses. It was possible to regard the determined values of the radii of the regions of inhomogeneity as the values of the radii of pores, and not of particles, and this result, moreover,

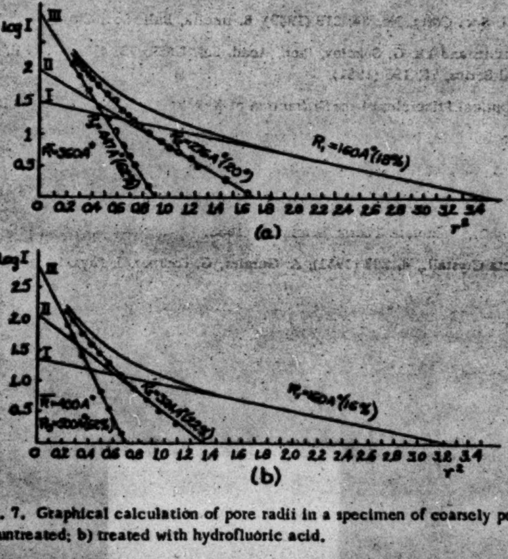


Fig. 7. Graphical calculation of pore radii in a specimen of coarsely porous glass: a) untreated; b) treated with hydrofluoric acid.

was in agreement with investigations on sorption. Only when the destruction of the submicroscopic structure of the specimen was so great that it ceased to be a porous glass —which occurred when it was completely broken down by the prolonged action of alkali— did the diffraction pattern change appreciably owing to the presence of scattering by nonporous particles.

TABLE 2

Calculation of Mean Radii of Dispersed Pores Before and After Treatment with Hydrofluoric Acid

	R_1 (A)	Content (%)	R_2 (A)	Content (%)	R_3 (A)	Content (%)	R_{av} (A)
Before treatment	160	18	276	20	447	62	360
After treatment	160	16	324	22	550	62	400

A further result of this investigation has been a deeper appreciation of the nature of the submicroscopic structure of porous glasses.

SUMMARY

1. The scattering intensities of specimens having the "direct" and "reverse" structures coincide precisely as far as the terms determining the zero-angle scattering: on the basis of the diffraction photograph it is impossible to make a choice between the two structures.

2. By the artificial enlargement of pores in specimens of porous glasses and calculation of the radii of the regions of inhomogeneity that account for the scattering of X-rays at low angles, it has been shown that such a method determines the radii of the pores, and not of the particles.

Received June 30, 1954

Institute of Silicate Chemistry of the
USSR Academy of Sciences

LITERATURE CITED

[1] M. Jellinek, E. Solomon, I. Fankuchen, Ind. Eng. Chem., An. Ed. 18, 172 (1946); P. Elkin, C. Shull, L. Roess, Ind. Eng. Chem., Ind. Ed., 37, 327 (1945); J. Am. Chem. Soc., 70, 1410 (1948).

[2] H. Brusset, Bull. Soc. Chim, No. 34, 319 (1949); B. Imelik, Bull. Soc. Chim., No. 12, 1232 (1950).

[3] E. A. Porai-Koshits and Yu. G. Sokolov, Proc, Acad. Sci. USSR, 72, 477 (1950); E. A. Porai-Koshits, Bull. Acad. Sci. USSR, Physical Series, 15, 195 (1951).

[4] R. W. James, Optical Principles of the Diffraction of X-Rays, Chapter IX, Foreign Lit. Press, 1950.

[5] M. I. Petrashen and E. A. Porai-Koshits, J. Expt. Theor. Phys., 21, 887 (1951).

[6] B. Walker and A. Guinier, Comptes rend., 235, 254 (1952).

[7] E. A. Porai-Koshits, Prog. Phys. Sci., 39, 573 (1949).

[8] E. A. Porai-Koshits, Doctorate Thesis, Leningrad, 1953.

[9] G. Fournet, Acta Crystall., 4, 293 (1951); A. Guinier, G. Fournet, J. Phys. Radium, 11, 516 (1950).

STRUCTURE OF SODIUM BOROSILICATE GLASSES IN ITS RELATION TO THE PHENOMENON OF OPALESCENCE

COMMUNICATION 1. INVESTIGATION OF THE OPALESCENCE OF GLASSES

D. I. Levin, S. P. Zhdanov, and E. A. Porai-Koshits

In spite of the fact that X-ray structural analysis is the most direct method for the determination of the structure of matter in any state of aggregation, practically no X-ray studies of the structure of vitreous materials have been made recently. We consider that this situation has arisen partly owing to an excess of enthusiasm for the application of so-called Fourier Analysis in the interpretation of diffuse and weak diffraction patterns [1]. The absence of other rigorous methods of interpretation and the simplicity of the application of the Fourier method of analysis —in which, with the aid of a single formula and without any obvious a priori assumptions concerning the structure of the material, the experimental intensity curve is transformed unequivocally into the curve for the radial distribution of atoms— have made this method extremely attractive. However, the averaging introduced in this mathematical treatment of diffraction patterns leads to the complete leveling of the fine structural details, and the resulting curves for the distribution of atoms cannot make any appreciable contribution to the theory of the vitreous state.

We consider that it is more useful to combine purely X-ray methods with other methods capable of giving valuable information concerning the structure of complex glasses. In this connection the selection of the object for investigation is of great importance. For this purpose we have selected alkali borosilicate glasses, which are very suitable owing to the considerable changes that occur in a number of their properties when small changes are made in their composition and thermal treatment; this applies particularly to their property of exhibiting opalescence in varying degree. Also, we have made use of their peculiar property of being susceptible to leaching with formation of so-called porous glasses, the properties of which are closely related to those of the original glasses. By a study of the opalescence of the latter and comparison of the results with those on the structure of the porous glasses, investigated by several independent methods, it is possible greatly to supplement the conclusions derived from a study based purely on X-ray examination.

In this paper, after an examination of present-day views on the causes of opalescence in sodium borosilicate glasses, we describe the results of the experimental study of opalescence. In a future communication we shall give the results of investigations into the structure of the porous products of the leaching of these glasses. Three independent methods of investigation (sorption, X-ray scattering at low angles, and electron microscope studies) are used.

In a third communication we shall make a comparison of the results of the investigations on the original and on the porous glasses and make an attempt to describe the structure of sodium borosilicate glasses on the basis of the experimental material obtained.

Survey of Existing Views on the Causes of Opalescence in Sodium Borosilicate Glasses

At the present time there is no single unified point of view with regard to the causes of the opalescence that occurs in certain glasses. The question of the causes of opalescence in sodium borosilicate glasses is even more obscure. According to patent specifications relating to the glass "Vycor" [2] and to a paper by one of the authors of these specifications [3], the opalescence of sodium borosilicate glasses is the result of their separation into two phases, one of which is siliceous, and the other is enriched in sodium oxide and boric anhydride. This separation of sodium borosilicate glasses of certain compositions into two phases occurs when they are maintained within a definite temperature range. Both phases are regarded as vitreous, since the investigation of opalescent sodium borosilicate glasses by means of the microscope or X-rays has not resulted in the detection of any crystalline formations. A similar view on the causes of opalescence in sodium borosilicate glasses has been expressed by Botvinkin [4], who maintains that, as a result of segregation during slow cooling, a colloidal solution of glass in glass is formed, and that it is possible in certain cases to observe, with the aid of the ultramicroscope, the presence of extremely fine particles of dispersed phase in glass that has undergone this segregation process.

Porai-Koshits [5] has investigated the scattering of X-rays by a sodium borosilicate glass of composition

Na 70-23.* By an analysis of the X-ray pattern, Poral-Koshits showed that there was an increase in the degree of order of the sodium borate component when the glass was held at the temperature of the opalescence zone. As is well-known, such thermal treatment results in an increase in the degree of opalescence. On this basis the author concluded that the opalescence of sodium borosilicate glasses results from the growth of borate crystallites. The disappearance of opalescence with further rise in temperature was explained as being due to the melting of these crystallites. It must be remembered, however, that, even when the glass is kept for a long time in the temperature range of the opalescence zone, the X-ray results indicate only slight amount of growth in the crystallites (not more than a few angstroms), whereas the intensity of the opalescence increases in this treatment by hundreds and thousands of times (see the next section). It appears doubtful whether such a small increase in the dimensions of the crystallites could be the cause of the extremely high observed increase in the intensity of opalescence.

Grebenshchikov and Molchanova [6], who made a detailed study of sodium borosilicate glasses, did not make any definite assertion regarding the causes of the opalescence of these glasses; they state, however, that "at temperatures corresponding to the appearance of opalescence, there is an increase in the size of the amicroscopic sodium borate crystallites, which form still larger, though still submicroscopic, crystals, which are directly in contact with one another". It would appear to follow from this quotation that the authors associate the appearance of opalescence with growth of sodium borate crystallites, i.e., that they hold the view expressed by Porai-Koshits in one of his earlier papers as discussed above.

Weyl, in a short review of the method of preparation of the glass "Vycor" and its properties [7], associates the opalescence of sodium borosilicate glasses with the separation of a previously homogeneous glass into two phases having different optical properties. According to Weyl, one of the phases is almost pure silica, and the other consists of alkali borates in a vitreous or finely crystalline form.

Sodium borosilicate glasses that do not show opalescence are regarded as homogeneous. This view, however, is contrary to the fact that porous glasses can be prepared from clear sodium borosilicate glasses that do not exhibit visible opalescence. It is evident that separation into two "phases" occurs also in the case of non-opalescent glasses. It has been shown by one of the authors of this paper [8, 9] that the difference in structure between opalescent and non-opalescent sodium borosilicate glasses cannot be regarded as fundamental, but is only a question of difference in degree of heterogeneity. Molchanova and coworkers [10, 11] consider that the opalescence of sodium borosilicate glasses is associated with the separation from the glass of some dispersed phase in such insignificant amount that this separation cannot affect the chemical properties of the glass.

An original view on the causes of the opalescence of sodium borosilicate glasses has recently been advanced by Abe [12]. In the opinion of this author, opalescence can occur in sodium borosilicate glasses only when the main constituents of the glass are supplemented by small amounts of modifying oxides having a cation valency of three or more, for example V_2O_5, MnO_2, As_2O_3, and Fe_2O_3. An addition of about 1% of such oxides is sufficient to cause opalescence. The temperature for maximum opalescence does not depend on the basic composition of the glass, but depends on the nature of the added modifying oxide. The author states that X-ray investigation of the opalescent glass provides a basis for the view that "ultramicroscopic crystals of cristobalite" are present. According to this investigator, opalescence does not result directly from the separation of sodium borosilicate glasses into two phases. Such a separation, however, appears to be a necessary prerequisite for the development of opalescence. The author considers that the direct cause of opalescence is the crystallization of cristobalite in the form of ultramicroscopic crystals, which can occur in a phase rich in SiO_2. The crystallization of cristobalite becomes possible only after the separation of the glass into two phases; such separation, therefore, must always precede opalescence. The ability of sodium borosilicate glasses to separation into two phases is to be explained by the tendency in such glasses to the formation of groupings consisting of one $[BO_4]$ tetrahedron surrounded by four $[BO_3]$ triangles.

Objections can be raised to these ideas of Abe concerning opalescence. It cannot be considered that the statement that opalescence occurs only when the main constituents of alkali borosilicate glasses are supplemented by additions of oxides having a cation valency of three or more is sufficiently well-grounded. It is known that oxides of tervalent metals encourage the transition of sodium borosilicate glasses into the opalescent state and that the addition of such oxides as MgO and CaO also greatly increases their opalescence. It is known also that sodium borosilicate glasses that contain no additives also show opalescence [6, 8, 2].

Also, it is impossible to agree with the author's assertion that the temperature for maximum opalescence does not depend on the basic composition of the glass. This is contradicted by data that we have at our disposal, and also by published data [6].

---

* Of the figures denoting the composition, the first is the silica content (mole-%), the second is the boron anhydride content (mole-%); the remainder consists of sodium oxide.

As regards the explanation of opalescence by the formation of ultramicroscopic crystals of cristobalite, this also cannot be regarded as satisfactory, since it is contrary to common sense and to experimental facts. In actual fact, the zone for the opalescence of the majority of sodium borosilicate glasses can be regarded as the temperature range 550-700° (see the next section). The crystallization of silica, however, generally begins at higher temperatures, so that between the two zones there is a zone of completely transparent glass. If the cause of opalescence were the crystallization of silica, it would be quite incomprehensible why the submicroscopic crystals of cristobalite formed should suddenly disappear when the temperature was raised and then appear again at a higher temperature. Only by prolonged maintenance of the glass at a temperature of about 700° can the two zones (opalescence and devitrification) be made to overlap, and they are easily distinguished visually: crystallization extends inward from a rough surface, whereas the opalescence of the glass occurs uniformly through the whole volume and the surface preserves its smoothness. Also, a more careful X-ray investigation by one of the authors of this paper [13] has shown that, when sodium borosilicate glasses are subjected to prolonged heating, sodium borates may crystallize out, but in no case was crystallization of silica detected within the opalescence zone.

It will be seen, therefore, that the causes of the opalescence of sodium borosilicate glasses still remain obscure. It must be pointed out that no quantitative study of the scattering of light by sodium borosilicate glasses has yet been carried out.

EXPERIMENTAL

Investigation of the Opalescence of Sodium Borosilicate Glasses

Rayleigh scattering in certain sodium borosilicate glasses is peculiar in that, under definite conditions of thermal treatment (keeping of the glass in the temperature range 550-700°), it increases until an opalescent state is attained. The intensity of the opalescence may vary within wide limits: from opalescence that is invisible to the unaided eye to such strong opalescence that the glass becomes opaque. The phenomenon of opalescence occurs in sodium borosilicate glasses having certain compositions. There can be no doubt that it is associated with peculiarities in the structures of these glasses and can be utilized not only in the study of their structures, but also in the elucidation of the question of the nature of Rayleigh scattering in glasses in general.

The procedure used in the study of the variation in the scattering by sodium borosilicate glasses when subjected to thermal treatment has been described previously [14]; it was as follows. The variation in the intensity and depolarization of the light scattered at 90° was studied by visual photometry. The intensity was measured with a star photometer, and depolarization was measured by Cornu's method with the aid of a Wollaston prism and a nicol. The sample under investigation was placed in a furnace provided with windows for the entry of the incident and exit of the scattered light. The intensity and depolarization measurements could be made without adjustment of the sample in the furnace. The light source was a SVD mercury lamp. In order to exclude fluorescence, a ZhS-8 glass filter, which cuts out the short-wave part of the spectrum up to 5000 A, was interposed in the incident beam. As a standard of scattering intensity, a sample of optical glass was used, and the intensity of the scattering produced by this was compared with the intensity of the molecular scattering of diethyl ether. Glasses of four different compositions were investigated: Na 70-23, Na 65-30, Na 60-37, and Na 60-30.

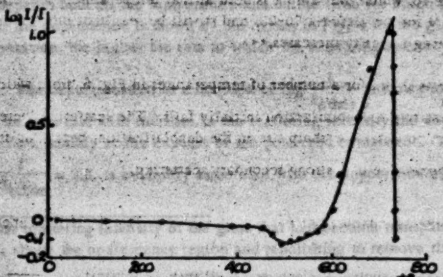


Fig. 1. Dependence of the intensity of the scattered light on temperature for the glass Na 70-23.

Fig. 1 shows the curve for the variation of scattering intensity with temperature for the glass Na 70-23, and this is typical for all of these glasses. The value of $\log \frac{I}{I_0}$ is plotted along the ordinate axis (I is the scattering intensity at a given temperature; I_0 is the scattering intensity at 20°. Measurements were made after the glass had been maintained at the given temperature for ten minutes. It will be seen from Fig. 1 that, according to the nature of the variation in the scattering, the following temperature ranges can be distinguished:

1. The low temperature range (room temperature to 550°), in which the scattering intensity diminishes with rise in temperature.

2. The range extending approximately from 550° to 700°, in which the scattering intensity rises steeply, i.e., the opalescence range.

3. The range in which opalescence disappears (above 700°): the scattering intensity falls to the values observed for optical glasses.*

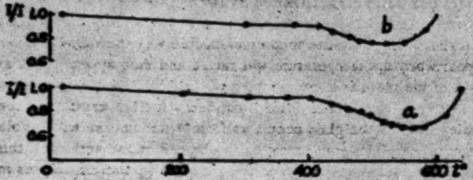


Fig. 2. Variation of the scattering intensity in the first temperature range for opalescent and non-opalescent samples of the glass Na 65-30:

a) $\frac{I_s}{I_{ether}}$ = 1000; b) $\frac{I_s}{I_{ether}}$ = 6.

At low temperatures the course of the curve for the variation in scattering intensity depends very little on the absolute value of the intensity. This can be clearly seen from Fig. 2, in which a comparison is made of such curves for opalescent and non-opalescent samples of the glass Na 65-30 (curves a and b, respectively). From Fig. 2 it will be seen also that for the opalescent glass the minimum of I/I_0 is more marked than that of the non-opalescent glass, and its position is displaced in the direction of higher temperatures. These phenomena evidently depend on the thermal history of the glass.

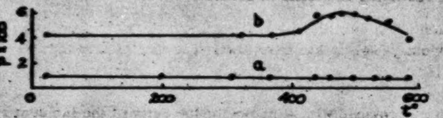


Fig. 3. Dependence of depolarization on temperature for opalescent and non-opalescent samples of the glass Na 65-30: a) $\frac{I_s}{I_{ether}}$ = 1000; b) $\frac{I_s}{I_{ether}}$ = 6.

It was further found that for non-opalescent glasses a rise in the depolarization ρ occurs in the region of the minimum value of I/I_0. For strongly opalescent glasses, for which the values of ρ are low (not greater than 0.01), no variation of ρ is observed. Fig. 3 shows the variation of the depolarization ρ with temperature for the same samples of glass Na 65-30. The rise in ρ with simultaneous fall in I/I_0 indicates that it is not the whole of the scattered light that is changing in intensity, but mainly its polarized component.

In the low-temperature range the variation in the scattering is almost reversible with respect to temperature. In the opalescence range the variation in the scattering is irreversible. The intensity of the scattering depends both on the temperature and on the time for which the sample is held at that temperature. The character of the dependence is shown by the curves in Fig. 4 for the glass Na 70-23, and it will be seen that the higher the temperature, the higher the rate at which the scattering intensity increases.**

The depolarization as a function of log $\frac{I}{I_{ether}}$ is shown for a number of temperatures in Fig. 5, from which it will be seen that with increase in the scattering intensity the depolarization initially falls. The scattering increases, therefore, mainly at the expense of the polarized component. The sharp rise in the depolarization, beginning from log $\frac{I}{I_{ether}} \approx 2.6$, is evidently associated with the appearance of a strong secondary scattering.

---

* The scattering intensity of the glass that had become transparent was determined after quenching from temperatures above the opalescence region and repolishing to remove the crystallized layer.

** For temperatures up to 638° the scattering intensity does not attain any definite limit. The limit log $\frac{I}{I_{ether}} \approx 3.8$, to which the scattering intensity tends at temperatures of 663° and higher, is an apparent limit. This limit is associated with the reduction in the intensity of the incident beam in its passage through a strongly scattering sample [14]. In our case, for a 15-mm length of sample, the effect of the reduction in the intensity of the incident beam on the measurements became apparent at values of log $\frac{I}{I_{ether}} > 2.5$.

At temperatures at which opalescence disappears, quantitative measurements become difficult: owing to their low viscosity the samples begin to flow and crystallization of SiO_2 sets in at the surface. Nevertheless, by a study of the direction of the change in scattering intensity it is possible to estimate a temperature range below which opalescence appears and above which it disappears. Fig. 6 shows the directions of the changes in scattering intensity for

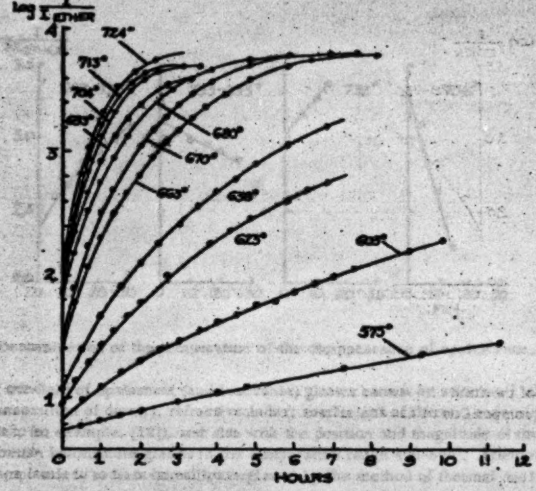


Fig. 4. Dependence of the scattering intensity on the time for which the glass Na 70-23 is held at different temperatures.

the same sample Na 70-23, which was held successively at a number of closely spaced temperatures. It will be seen from Fig. 6 that the range sought comprises not more than 2-3°, so that in a certain sense we may speak of a critical temperature for the disappearance of opalescence. It was found that the value of the critical temperature may vary, not only for glasses of different compositions, but also for glasses of the same composition, but from different meltings.

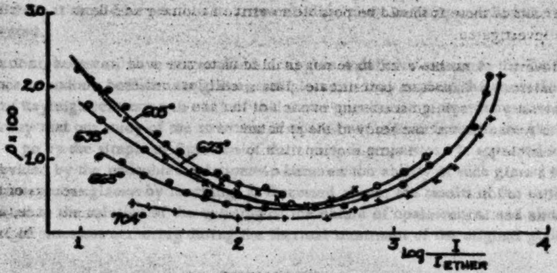


Fig. 5. Dependence of the depolarization on the scattering intensity for the glass Na 70-23.

In sodium borosilicate glasses that do not show opalescence, for example Na 60-20, and in optical (flint) glasses, the phenomena described here, in particular the fall in scattering intensity with temperature in the range 20-550°, are not found. This constitutes evidence for the presence of structural peculiarities in glasses capable of developing opalescence. Examination of the compositions of such glasses shows that they belong to the group of ternary glasses that are able to form porous products when subjected to leaching by acid solutions [6, 4, 3]. The field of the compositions of these glasses, however, does not coincide with any definite phase field of the ternary melting-point diagram, but covers only a part of the silica field. The crystallizing tendency of sodium borosilicate glasses is also not associated in any way with the boundaries of this field, and the phenomena described here, in particular the sharp rise in opalescence at temperatures from 550° to 700°, cannot be explained by incipient crystallization processes.

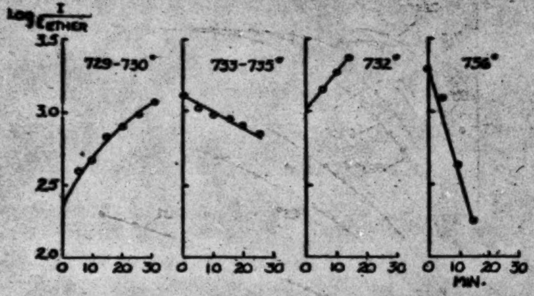


Fig. 6. Determination of the temperature of the disappearance of opalescence.

The boundaries of the field of opalescent (and leachable) glasses cannot be associated with any effects in the smooth variation with composition of density, refractive index, coefficient of thermal expansion, and so on, at temperatures below 1000° (see, for example, [12]), and also with the position and magnitude of the diffuse endothermic effect observed for all sodium borosilicate glasses in the temperature range 400-600°. Attempts to establish the presence of chemical compounds in sodium borosilicate glasses by the method of thermal analysis have not yielded positive results [13].

The results of the investigation described above show, above all, the unsatisfactory nature of the accepted explanations of Rayleigh scattering in glasses as caused by "frozen-in" density fluctuations, deformations, or fortuitous optical heterogeneities. These results have established an undoubted relationship between the intensity of Rayleigh scattering and the structure of the investigated glasses. The latter, in its turn, has been found to be dependent not only on the composition of the glasses, but also on their thermal treatment, or on the previous thermal history of the samples. At the same time we have succeeded in establishing certain quite general regularities characteristic of all of the compositions investigated (for example, the existence of three temperature zones for the changes in the scattering intensity, the reversibility of these changes in the first zone, their nonreversibility in the opalescence zone, and so on), and on the basis of these it should be possible to arrive at some more definite conclusions regarding the structure of the glasses investigated.

Even these investigations, however, have not enabled us to give a definite answer to the fundamental question of the causes of opalescence in sodium borosilicate glasses; still less can they explain the anomalous temperature variation of the intensity of Rayleigh scattering in each of the above-mentioned temperature zones. For the answer to this question it is necessary that our study of the structure of opalescent sodium borosilicate glasses should go deeper than it is possible to go by the simple comparison of their various properties. It appeared to us that a promising line of approach is provided by the undoubted relationship between the ability of such glasses to become opalescent and their ability to form porous glasses by leaching, as discussed above; the results of the study of the structure of the latter could be applied to the solution of the question of the nature of opalescence, and also to the elucidation of the essential nature of processes occurring during the thermal treatment of the original glasses.

SUMMARY

1. Existing views on the causes of opalescence in sodium borosilicate glasses are mutually contradictory and are not based on the quantitative study of the scattering of light in these glasses.

2. Investigation of Rayleigh scattering in sodium borosilicate glasses has established beyond doubt that there is a relationship between the scattering intensity and the structure of the glass. It has been shown that there are three temperature zones characterized by the way in which the intensity varies: a zone in which the intensity falls with rise in temperature, the opalescence zone, and the zone in which opalescence disappears.

3. In order to interpret the observed regularities, a deeper study of the structure of sodium borosilicate glasses will be necessary. A promising line of approach can be based on the relationship between the ability of sodium borosilicate glasses to become opalescent and their ability to form porous glasses by leaching, the structure of the latter being open to investigation by several independent methods.

Received April 2, 1954

Institute of Silicate Chemistry of the
USSR Academy of Sciences

LITERATURE CITED

[1] M. L. Petrashen and E. A. Porai-Koshits, J. Expt. Theor. Phys., 21, 887 (1951).

[2] Review of the Patents of the Corning Glass Works relating to "Vycor" glass, J. Soc. Glass Techn., 23, 352 (1939); Bull. Am. Cer. Soc., 18, 270 (1939); C. 1937, 2, 3062; Glass Ind., 21, 482 (1940).

[3] M. E. Nordberg, J. Am. Cer., Soc., 27, 299 (1944).

[4] O. K. Botvinkin, Light Industry, No. 3, 20 (1941).

[5] E. A. Porai-Koshits, Proc. Acad. Sci. USSR, 36, 285 (1942); J. Gen. Chem., 12, 196 (1942).

[6] I. V. Grebenshchikov and O. S. Molchanova, J. Gen. Chem., 12, 588 (1942).

[7] W. A. Weyl, Ang. Chem., 63, 86 (1952).

[8] S. P. Zhdanov, Thesis, Leningrad, 1950.

[9] S. P. Zhdanov, Proc. Acad. Sci. USSR, 82, 281 (1952).

[10] O. S. Molchanova and V. M. Serebryakova, Trans. State Optical Institute, 23, 3 (1953).

[11] O. S. Molchanova and L. A. Pakhomova, Trans. State Optical Institute, 23, 13 (1953).

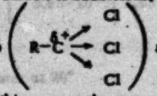
[12] T. Abe, J. Am. Cer. Soc., 35, 284 (1952).

[13] E. A. Porai-Koshits, Doctorate Thesis, Leningrad, 1953.

[14] D. I. Levin, Thesis, Leningrad, 1951.

PREPARATION OF CARBOXYLIC ACIDS OF STRUCTURE $CCl_3(CH_2)_nCOOH$ AND CCl_2=$CH(CH_2)_nCOOH$, AND THEIR DISSOCIATION CONSTANTS

A. N. Nesmeyanov, L. I. Zakharkin and R. Kh. Freidlina

Compounds containing the trichloromethyl group have now become readily accessible by the addition reactions given by chloroform, carbon tetrachloride, and bromotrichloromethane with olefins. According to its structure, the trichloromethyl group  must be classified with electron-acceptor substituents (orienting groups of the second kind). In this respect the group is of particular interest, since it does not contain double bonds and so cannot be in π,π-conjugation with double bonds or with the benzene ring. The investigation of the orienting effect of the trichloromethyl group for electrophilic substitution in the aromatic nucleus has yielded contradictory results. Thus, the trichloromethyl group of benzotrichloride orients meta in nitration and ortho-para in chlorination [1].

At attempt to determine the orienting effect of the trichloromethyl group on the electrophilic addition of hydrogen bromide to 3,3,3-trichloropropene showed that in absence of catalysts no reaction occurred, while in presence of $AlCl_3$ the 3,3,3-trichloropropene isomerized into 1,1,3-trichloropropene [2]. It has also not been found possible to detect any tendency of the trichloromethyl group in saturated polychloro hydrocarbons to enter into reaction with nucleophilic reagents, probably owing to the screening of the center of nucleophilic attack by the three chlorine atoms [3]. Up to the present, therefore, there are no direct experimental data on which to base the classification of the trichloromethyl group as an electron-accepting substituent. It is thus of interest to study the effect of the trichloromethyl group on other functional groups. Herein, we describe the synthesis of a number of carboxylic acids $CCl_3(CH_2)_nCOOH$ and CCl_2=$CH-(CH_2)_nCOOH$, and we give their dissociation constants, which have been determined in order to show the effect of the CCl_3 and CCl_2=CH groups on the carboxyl group for varying lengths of intervening chain. The only previously known members of the series of CCl_3-containing carboxylic acids are trichloroacetic, 4,4,4-trichlorobutyric [4], and 7,7,7-trichloroheptanoic [5] acids. Attempts to prepare 3,3,3-trichloropropionic acid by the hydrolysis of its ethyl ester were not successful [6]. Of the carboxylic acids containing the CCl_2=CH group, 3,3-dichloroacrylic and 4,4-dichloro-3-butenoic [7] acids have been described. We have synthesized the acids $CCl_3(CH_2)_nCOOH$ (n = 2-6) and CCl_2=$CH-(CH_2)_nCOOH$ (n = 1-6).

5,5,5-Trichlorovaleric acid was prepared according to the scheme:

$$CCl_3(CH_2)_4Cl \rightarrow CCl_3(CH_2)_4OCOCH_3 \rightarrow CCl_3(CH_2)_4OH \rightarrow CCl_3(CH_2)_3COOH.$$

Oxidation of the trichloropentanol was effected with chromic anhydride in glacial acetic acid, when, in addition to 5,5,5-trichlorovaleric acid, 5,5,5-trichlorovaleraldehyde and the 5,5,5-trichloropentyl ester of 5,5,5-trichlorovaleric acid were formed. 6,6,6-Trichlorohexanoic acid and 8,8,8-trichlorooctanoic acid were prepared in accordance with the scheme:

$$CCl_3(CH_2)_nCl \rightarrow CCl_3(CH_2)_nCN \rightarrow CCl_3(CH_2)_nCOOH,$$

(n = 4 and 6).

When 8,8,8-trichlorooctanenitrile was hydrolyzed with concentrated sulfuric acid, suberic acid was obtained in almost quantitative yield. 5,5-Dichloro-4-pentenoic, 7,7-dichloro-6-heptenoic, and 9,9-dichloro-8-nonenoic acids were prepared according to the scheme:

$$CCl_2{=}CH(CH_2)_nCl + CH_2(COOC_2H_5)_2 \xrightarrow{C_2H_5ONa} CCl_2{=}CH-(CH_2)_nCH(COOC_2H_5)_2 \rightarrow CCl_2{=}CH-(CH_2)_{n+1}COOH,$$

(n = 1, 3 and 5).

An attempt to prepare 5,5-dichloro-4-pentenoic acid by the oxidation of 5,5-dichloro-4-penten-1-ol did not give the desired result owing to the action of the oxidizing agent on the CCl_2=CH group. 6,6-Dichloro-5-hexenoic and 8,8-dichloro-7-octenoic acids were prepared according to the scheme:

$$CCl_2{=}CH-(CH_2)_nCl \rightarrow CCl_2{=}CH-(CH_2)_n\,CN \rightarrow CCl_2{=}CH-(CH_2)_nCOOH,$$

(n = 3 and 5).

All of the CCl_3-containing acids obtained are low-melting crystalline substances; the acids containing the CCl_2=CH group are liquids. Owing to the insolubility of the higher members of the series in water, the dissociation constants were determined in a 50% by weight methanol solution for all of the acids, and also in water for the first two members of each series. The results obtained are given in Tables 1 and 2.

TABLE 1

Dissociation Constants in a 50% by Weight Methanol Solution at 25°

n	2	3	4	5	6	7
$CCl_3(CH_2)_nCOOH$	$4.6 \cdot 10^{-6}$	$1.5 \cdot 10^{-6}$	$1.25 \cdot 10^{-6}$	$9.55 \cdot 10^{-7}$	$8.95 \cdot 10^{-7}$	
$CCl_2{=}CH{-}(CH_2)_{n-1}COOH$	$5.95 \cdot 10^{-6}$	$1.45 \cdot 10^{-6}$	$9.25 \cdot 10^{-7}$	$8.75 \cdot 10^{-7}$	$7.75 \cdot 10^{-7}$	$6.3 \cdot 10^{-7}$

TABLE 2

Dissociation Constants in Water at 20°

$CCl_3CH_2CH_2COOH$	$6.2 \pm 0.1 \cdot 10^{-5}$	$CCl_2{=}CH{-}CH_2{-}COOH$	$9.1 \pm 0.1 \cdot 10^{-5}$
$CCl_3CH_2CH_2CH_2COOH$	$3.0 \pm 0.1 \cdot 10^{-5}$	$CCl_2{=}CH{-}CH_2{-}CH_2{-}COOH$	$2.7 \pm 0.1 \cdot 10^{-5}$

For comparison we may cite the dissociation constants of butyric and valeric acids at 18°, which are $1.53 \cdot 10^{-5}$ and $1.51 \cdot 10^{-5}$, respectively [8]; of 4-chlorobutyric and 5-chlorovaleric acids at 25°, which are $3 \cdot 10^{-5}$ and $2.04 \cdot 10^{-5}$, respectively [9]; and of 4,4,4-trifluorobutyric and 5,5,5-trifluorovaleric acids at 25°, which are $6.98 \cdot 10^{-5}$ and $3.2 \cdot 10^{-5}$, respectively [10, 11]. The inductive effect of the CCl_3 group results in a quite definite increase in the acidity, as compared with the unsubstituted acids, even in 5,5,5-trichlorovaleric acid, in which the CCl_3 and COOH groups are separated by three methylene groups. Increase in the number of chlorine atoms from one to three also results in an appreciable increase in the dissociation constant in the case of butyric and valeric acids. The difference in the effects of the trifluoro- and trichloro-methyl groups falls with increase in the number of methylene groups, and it becomes inappreciable already for valeric acid. The dissociation constants change greatly as we pass from the C_4 to the C_5 acids, and then change very little. It is interesting to note that 4,4-dichloro-3-butenoic acid has a higher dissociation constant than 4,4,4-trichlorobutyric acid, i.e., two chlorine atoms in the first acid have a greater effect than three chlorine atoms in the second; but in the succeeding acids the relationship is reversed. This behavior is probably to be associated with the fact that in 4,4-dichloro-3-butenoic acid the CCl_2=CH and COOH groups are separated by only one CH_2 group. For the acids studied, no feature can be discerned in the mode of variation of the dissociation constants that can be associated with the oddness or evenness of the number of methylene groups separating the two functional groups.

EXPERIMENTAL

The dissociation constants were calculated from the pH values of partly neutralized solutions of the acids; the activity coefficient was taken as unity. The pH measurements were carried out on an LP-4 potentiometer with glass and calomel electrodes. The acids containing a dichlorovinyl group were vacuum-distilled in a current of nitrogen before the determinations.

4,4,4-Trichlorobutyric acid was prepared by hydrolysis of the corresponding nitrile [4] with a mixture of acetic and hydrochloric acids; b.p. 102-103° (2.5 mm); m.p. 55°; the literature [4] gives m.p. 55°. The anilide of 4,4,4-trichlorobutyric acid has m.p. 159-160° (from benzene-ligroin).

Found %: N 5.11 5.19
$C_{10}H_{10}Cl_3NO$. Calculated %: N 5.25

5,5,5-Trichloro-1-pentanol acetic ester. A solution of 42 g of 1,1,1,5-tetrachloropentane, 25 g of potassium acetate, and 1 g of potassium iodide in 80 ml of glacial acetic acid was heated under reflux for 18 hours. The mixture was cooled, water was added, and the oil that separated was extracted with chloroform. The chloroform solution was washed with sodium carbonate solution and dried with sodium sulfate. The solvent was removed, and the residue was vacuum-distilled, when it yielded 37.4 g (80%) of the acetic ester of 5,5,5-trichloro-1-pentanol, b.p. 99-100° (3.5 mm); n_D^{20} 1.4700; d_4^{20} 1.2859; found MR 50.66; calculated MR 50.78.

Found %: C 35.62; 35.77; H 4.93; 4.91
$C_7H_{11}Cl_3O_2$. Calculated %: C 35.97; H 4.71

5,5,5-Trichloro-1-pentanol. A solution of 70.5 g of 5,5,5-trichloro-1-pentanol acetic ester in 60 ml of methanol containing 1 ml of concentrated hydrochloric acid was set aside for 24 hours. The excess of methanol and methyl acetate was then distilled off from a water bath. The residue was again dissolved in 60 ml of methanol containing 1 ml of concentrated hydrochloric acid, and the solution was heated under reflux for three hours. The methanol was removed, and the residue was vacuum-distilled, when it yielded 57 g (99%) of 5,5,5-trichloropentanol, b.p. 112-113° (10 mm); n_D^{20} 1.4897; d_4^{20} 1.3431; found MR 41.20; calculated MR 41.41.

Found %: C 31.07; 31.31; H 4.84; 4.90
$C_5H_9Cl_3O$. Calculated %: C 31.38; H 4.70

5,5,5-Trichlorovaleric acid. Chromic anhydride (7 g) was added slowly to a stirred cooled solution of 19 g of 5,5,5-trichloro-1-pentanol in 50 ml of glacial acetic acid, and the mixture was set aside for four hours at room temperature. Water was then added, and the oil that separated was extracted with chloroform. The chloroform extract was washed with sodium carbonate solution and dried with sodium sulfate. When the alkaline solution was acidified, 5,5,5-trichlorovaleric acid was precipitated and was collected on the filter and washed with water. A yield of 4.5 g of acid, m.p. 65-66° (from petroleum ether) was obtained.

Found %: C 29.36; 29.27; H 3.48; 3.65
$C_5H_7Cl_3O_2$. Calculated %: C 29.19; H 3.40

The anilide of 5,5,5-trichlorovaleric acid has m.p. 117-118° (from benzene-ligroin).

Found %: N 4.99; 4.85
$C_{11}H_{12}Cl_3NO$. Calculated %: N 4.99

Two fractions were separated when the chloroform solution was vacuum-distilled: Fraction I, b.p. 103-104° (8 mm), 3.2 g; and Fraction II, b.p. 164-165° (1.5 mm), 7.1 g. Fraction I was 5,5,5-trichlorovaleraldehyde, n_D^{20} 1.4890; d_4^{20} 1.3662; found MR 40.06; calculated MR 39.91.

Found %: C 31.51; 31.50; H 3.91; 3.85
$C_5H_7Cl_3O$. Calculated %: C 31.66; H 3.70

Its dinitrophenylhydrazone melted at 133-134°.

Found %: Cl 28.80; 28.77
$C_{11}H_{11}Cl_3N_4O_4$. Calculated %: Cl 28.82

Fraction II was the 5,5,5-trichloropentyl ester of 5,5,5-trichlorovaleric acid, n_D^{20} 1.500; d_4^{20} 1.4060; found MR 79.34; calculated MR 79.24.

Found %: C 44.19; 44.21; H 5.01; 5.20
$C_{10}H_{14}Cl_6O_2$. Calculated %: C 44.03; H 5.13

6,6,6-Trichlorohexanoic acid. A solution of 20 g of 6,6,6-trichlorohexanenitrile in a mixture of acetic and hydrochloric acids (80 ml of glacial acetic acid, 30 ml of concentrated hydrochloric acid, and 20 ml of water) was heated under reflux for eight hours. Part of the acetic acid was then driven off under reduced pressure, water was added to the residue, and the oil that separated was extracted with chloroform. The product was 18.1 g (82%) of 6,6,6-trichlorohexanoic acid, b.p. 114-115° (1 mm); m.p. 50-51° (from petroleum ether).

Found %: C 33.03; 32.90; H 4.04; 4.08
$C_6H_9Cl_3O_2$. Calculated %: C 32.80; H 4.10

The anilide of 6,6,6-trichlorohexanoic acid melts at 109-110°

Found %: N 4.96; 4.84
$C_{12}H_{14}Cl_3NO$. Calculated %: N 4.75

7,7,7-Trichloroheptanoic acid was prepared as previously described [5].

The anilide of 7,7,7-trichloroheptanoic acid melts at 98-99°.

Found %: N 4.58; 4.58
$C_{13}H_{16}Cl_3NO$. Calculated %: N 4.54

8,8,8-Trichlorooctanenitrile. A mixture of 90 g of 1,1,1,7-tetrachloroheptane, 30 g of sodium cyanide in 60 ml of water, and 250 ml of alcohol was heated with stirring for twelve hours. The alcohol was driven off from a water bath, water was added to the residue, and the oil formed was extracted with chloroform. The chloroform solution was washed with water and dried with calcium chloride. The product was 62 g (72.5%) of 8,8,8-trichlorooctanenitrile, b.p. 123-125° (2.5 mm); n_D^{20} 1.4787; d_4^{20} 1.2097; found MR 53.53; calculated MR 53.56.

Found %: N 6.18; 6.28
$C_8H_{12}Cl_3N$. Calculated %: N 6.12

Hydrolysis of 8,8,8-trichlorooctanenitrile. A solution of 15 g of 8,8,8-trichlorooctanenitrile in 30 ml of concentrated hydrochloric acid was heated with stirring in a boiling water bath for one hour. Water (30 ml) was added, and the solution was boiled under reflux for 30 minutes. On cooling, the solution yielded a precipitate of suberic acid, which was washed on the filter with cold water. The yield of acid, m.p. 139-140°, was 10.7 g (94%).

8,8,8-Trichlorooctanoic acid. A solution of 23 g of 8,8,8-trichlorooctanenitrile in a mixture of 80 ml of glacial acetic acid, 30 ml of concentrated hydrochloric acid, and 20 ml of water was heated under reflux for ten hours. The usual treatment yielded 19.6 g (79%) of 8,8,8-trichlorooctanoic acid, b.p. 139-140° (1.0 mm); m.p. 38-39° (from petroleum ether).

Found %: C 38.94; 39.02; H 5.37; 5.20
$C_8H_{13}O_2Cl_3$. Calculated %: C 38.82; H 5.25

The anilide of 8,8,8-trichlorooctanoic acid melts at 108-109°.

Found %: N 4.22; 4.33
$C_{14}H_{18}Cl_3NO$. Calculated %: N 4.34

4,4-Dichloro-3-butenoic acid was prepared as previously described [7].

The anilide of 4,4-dichloro-3-butenoic acid melts at 82-83°.

Found %: N 6.15; 6.18
$C_{10}H_9Cl_2NO$. Calculated %: N 6.08

5,5-Dichloro-4-penten-1-ol acetic ester. A solution of 65 g of 1,1,5-trichloro-1-pentene [4], 45 g of potassium acetate, and 1.5 g of potassium iodide in 150 ml of glacial acetic acid was heated under reflux for 16 hours. Water was added to the mixture, when cool, and the oil formed was extracted with chloroform. The chloroform solution was washed with a solution of sodium carbonate and dried with sodium sulfate. The product was 62.1 g (84%) of the acetic ester of 5,5-dichloro-4-penten-1-ol, b.p. 58° (1.5 mm); n_D^{20} 1.4690; d_4^{20} 1.2095; found MR 45.35; calculated MR 45.54.

Found %: C 42.83; 42.87; H 5.18; 5.42
$C_7H_{10}Cl_2O_2$. Calculated %: C 42.69; H 5.08

5,5-Dichloro-4-penten-1-ol. A solution of 53 g of the acetic ester of 5,5-dichloro-4-penten-1-ol and 1 ml of concentrated hydrochloric acid in 80 ml of methanol was heated under reflux for six hours. The methanol and methyl acetate were distilled off from a water bath, and 1 ml of concentrated hydrochloric acid and 60 ml of methanol were added to the residue. The solution was heated for a further three hours, and yielded 38 g (93%) of 5,5-dichloro-4-penten-1-ol, b.p. 59-60° (2.5 mm); n_D^{20} 1.4923; d_4^{20} 1.2452; found MR 36.14; calculated MR 36.18.

Found %: C 38.91; 38.95; H 5.22; 5.19
$C_5H_8Cl_2O$. Calculated %: C 38.75; H 5.16

5,5-Dichloro-4-pentenoic acid. A solution of 23.5 g of the diethyl ester of (3,3-dichloroallyl)malonic acid in a mixture of 70 ml of glacial acetic acid, 25 ml of concentrated hydrochloric acid, and 25 ml of water was boiled under reflux for eight hours. The mixture was cooled, water was added, and the oil formed was extracted with chloroform. The chloroform was distilled off from a water bath, and the residue was heated at 170-180° until evolution of carbon dioxide ceased (30 minutes), and was then dissolved in dilute caustic potash solution. The alkaline solution was extracted with ether and then acidified with hydrochloric acid. The oil that separated was extracted with chloroform. The chloroform solution was washed with water and dried with calcium chloride. After removal of chloroform, the residue was vacuum-distilled in a current of nitrogen, when it yielded 10.6 g (72%) of 5,5-dichloro-4-pentenoic acid, b.p. 93-94° (1 mm); n_D^{20} 1.4898; d_4^{20} 1.3546; found MR 36.06; calculated MR 3609.

Found %: C 35.61; 35.64; H 3.56; 3.59,
$C_5H_6Cl_2O_2$. Calculated %: C 35.52; H 3.55

The anilide of 5,5-dichloro-4-pentenoic acid melts at 72-73° (from benzene-ligroin).

Found %: N 5.60; 5.50
$C_{11}H_{11}Cl_2NO$. Calculated %: N 5.73

6,6-Dichloro-5-hexenoic acid was prepared in 92% yield by hydrolysis of the corresponding nitrile [6] with a mixture of acetic and hydrochloric acids; b.p. 139-140° (8 mm); n_D^{20} 1.4895; d_4^{20} 1.2967; found MR 40.77; calculated MR 40.71.

Found %: C 39.17; 39.10; H 4.29; 4.34
$C_6H_8Cl_2O_2$. Calculated %: C 39.32; H 4.37

The anilide of 6,6-dichloro-5-hexenoic acid melts at 63-64° (from benzene-ligroin).

Found %: N 5.60; 5.45
$C_{12}H_{13}Cl_2NO$. Calculated %: N 5.42

Diethyl ester of 5,5-dichloro-4-pentenylmalonic acid. 1,1,5-Trichloro-1-pentene (37g) was heated for ten hours with sodiomalonic ester prepared from 35 g of malonic ester and 4.7 g of sodium in 60 ml of absolute alcohol. When the mixture was cool, water was added, and the oil that separated was extracted with chloroform. The product was 37.2 g (60%) of the diethyl ester of 5,5-dichloro-4-pentenylmalonic acid, b.p. 122-123° (1.5 mm); n_D^{20} 1.4650; d_4^{20} 1.1693; found MR 70.22; calculated MR 70.19.

Found %: C 48.75; 48.60; H 6.04; 6.04
$C_{12}H_{18}Cl_2O_4$. Calculated %: C 48.50; H 6.06

7,7-Dichloro-6-heptenoic acid was obtained in 90% yield by hydrolysis of the diethyl ester of 5,5-dichloro-4-pentenylmalonic acid with a mixture of acetic and hydrochloric acids, the procedure being similar to that used for the preparation of 5,5-dichloro-4-pentenoic acid; b.p. 120-121° (1 mm); n_D^{20} 1.4872; d_4^{20} 1.2479; found MR 45.41; calculated MR 45.33.

Found %: C 42.71; 42.62; H 5.02; 4.92
$C_7H_{10}Cl_2O_2$. Calculated %: C 42.64; H 5.07

The anilide of 7,7-dichloro-6-heptenoic acid melts at 68-69° (from benzene-ligroin).

Found %: N 5.19; 5.22
$C_{13}H_{15}Cl_2NO$. Calculated %: N 5.14

8,8-Dichloro-7-octenenitrile. Heating of 30 g of 1,1,7-trichloro-1-heptene with 11 g of sodium cyanide in 70 ml of alcohol and 20 ml of water for twelve hours yielded 21.1 g (73%) of 8,8-dichloro-7-octenenitrile, b.p. 99-100° (1.5 mm); n_D^{20} 1.4840; d_4^{20} 1.1410; found MR 48.04; calculated MR 48.23.

Found %: N 7.14; 7.12
$C_8H_{11}Cl_2N$. Calculated %: N 7.29

8,8-Dichloro-7-octenoic acid was prepared in 80% yield by hydrolysis of 8,8-dichloro-7-octenenitrile with a mixture of acetic and hydrochloric acids; b.p. 128-129° (1 mm); n_D^{20} 1.4859; d_4^{20} 1.2120; found MR 49.97; calculated MR 50.04.

Found %: C 45.66; 45.74; H 5.85; 5.90
$C_8H_{12}Cl_2O_2$. Calculated %: C 45.52; H 5.68

The anilide of 8,8-dichloro-7-octenoic acid melts at 62-63° (from benzene-ligroin).

Found %: N 4.97; 5.01
$C_{14}H_{17}Cl_2NO$. Calculated %: N 4.89

Diethyl ester of 7,7-dichloro-6-heptenylmalonic acid. 1,1,7-Trichloro-1-heptene (40 g) was heated for ten hours with sodiomalonic ester prepared from 35 g of malonic ester and 4.6 g of sodium in 70 ml of absolute alcohol. The product was 41.1 g (65%) of the diethyl ester of 7,7-dichloro-6-heptenylmalonic acid, b.p. 142-143° (1 mm); n_D^{20} 1.4663; d_4^{20} 1.1341; found MR 79.41; calculated MR 79.43.

Found %: C 51.44; 51.40; H 6.63; 6.59
$C_{14}H_{22}Cl_2O_4$. Calculated %: C 51.69; H 6.76

9,9-Dichloro-8-nonenoic acid was prepared in 82% yield by hydrolysis of the diethyl ester of 7,7-dichloro-6-heptenylmalonic acid with a mixture of acetic and hydrochloric acids, the procedure being similar to that used for the preparation of 5,5-dichloro-4-pentenoic acid; b.p. 132-133° (1 mm); n_D^{20} 1.4848; d_4^{20} 1.1806; found MR 54.60; calculated MR 54.68.

Found %: C 47.91; 47.89; H 6.23; 6.17
$C_9H_{14}Cl_2O_2$. Calculated %: C 48.00; H 6.22

The anilide of 9,9-dichloro-8-nonenoic acid melts at 54-55° (from benzene-ligroin).

Found %: N 4.77; 4.63
$C_{15}H_{19}Cl_2NO$. Calculated %: N 4.66

SUMMARY

1. The acids $CCl_3(CH_2)_nCOOH$ (n = 2-6) and $CCl_2{=}CH{-}(CH_2)_nCOOH$ (n = 1-6) have been prepared, and their dissociation constants have been measured potentiometrically.

2. It has been found that the CCl_3 and $CCl_2{=}CH$ groups have appreciable effects on the dissociation constants of the acids; these effects fall off regularly as the length of the chain separating these groups from carboxyl increases.

3. It has been found that 4,4-dichloro-3-butenoic acid has a higher dissociation constant that 4,4,4-trichlorobutyric acid, whereas in the succeeding acids in the two series the reverse relationship holds.

4. It has been found that in the higher ω,ω,ω-trihalo carboxylic acids, the CCl_3 and CF_3 groups have approximately the same effect on the dissociation constant.

Received March 31, 1954

Institute of Heteroorganic Compounds
of the USSR Academy of Sciences

LITERATURE CITED

[1] W. M. Latimer, C. W. Porter, J. Am. Chem. Soc., 52, 206 (1930).

[2] A. N. Nesmeyanov, R. Kh. Freidlina, and V. I. Firstov, Proc. Acad. Sci. USSR, 78, 717 (1951); Bull. Acad. Sci. USSR, Div. Chem. Sci., 1951, 503.

[3] A. N. Nesmeyanov, R. Kh. Freidlina, and L. I. Zakharkin, Proc. Acad. Sci. USSR, 96, 87 (1954).

[4] H. A. Bruson, W. Niederhauser, T. Riener, W. F. Hester, J. Am. Chem. Soc., 67, 601 (1945).

[5] A. N. Nesmeyanov, L. I. Zakharkin, and R. Kh. Freidlina, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 1, 34.*

[6] F. Brown, W. K. Musgrave, J. Chem. Soc., 1953, 2087.

[7] A. N. Nesmeyanov, L. I. Zakharkin, V. N. Kost, and R. Kh. Freidlina, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 4, 604.**

[8] E. Larson, B. Adell, Z. Phys. Chem., 156, 352 (1931).

[9] D. M. Lichty, Ann., 219, 369 (1901).

[10] A. L. Henne, Ch. J. Fox, J. Am. Chem. Soc., 75, 2323 (1951).

[11] A. L. Henne, Ch. J. Fox, J. Am. Chem. Soc., 75, 5750 (1953).

---

* See Consultants Bureau Translation, page 27.

** " " " " " 515.

REACTIONS OF ORGANOMAGNESIUM COMPOUNDS WITH POTASSIUM AND TRIETHYLOXONIUM FLUOBORATES

A. N. Nesmeyanov, V. A. Sazonova, G. S. Liberman and L. I. Emelyanova

For the synthesis of full organoboron compounds, it has been usual to apply the reaction of organomagnesium compounds with boric esters or halogen derivatives of boron. Of the boron halides, the trifluoride is the most frequently used (in the form of its etherate). It is known that inorganic and organic boron derivatives tend to form complexes. Recently, Wittig and coworkers [1] have shown that in ether solution triphenylborine combines with phenyllithium:

$$(C_6H_5)_3B + C_6H_5Li \rightarrow LiB(C_6H_5)_4.$$

Lithium tetraphenylboron can be obtained also by the action of BF_3 on C_6H_5Li. For purposes of analysis the authors used the reaction of lithium tetraphenylboron with mercuric chloride, which goes quantitatively with formation of C_6H_5HgCl, HCl, H_3BO_3, and LiCl. When a potassium salt is added to an aqueous solution of $LiB(C_6H_5)_4$, the water-insoluble potassium tetraphenylboron is formed:

$$LiB(C_6H_5)_4 + K^+ \rightarrow KB(C_6H_5)_4 + Li^+.$$

When lithium tetraphenylboron is treated with cupric chloride (in equimolecular amount), the salt is decomposed with formation of biphenyl and triphenylborine. When a large excess of lithium tetraphenylboron is used, copper tetraphenylboron is obtained. The reaction is carried out in ether solution over a period of a week. Compounds of the type MBR_4 have as yet received little study, and such work as has been done has been largely confined to the phenyl derivative.

In the present paper we propose a simpler and more convenient method for the synthesis of trimethylborine and certain tetraarylboron salts. It has been found that potassium tetraphenylboron is readily prepared in ether by the action of phenylmagnesium bromide on potassium fluoborate:

$$4C_6H_5MgBr + KBF_4 \rightarrow KB(C_6H_5)_4 + 4MgBrF.$$

Reaction with p-tolylmagnesium bromide is somewhat more difficult.

In comparison with $KB(C_6H_5)_4$, potassium tetra-p-tolylboron is considerably less soluble in organic solvents (acetone, chloroform, and pyridine). Both the tetraphenyl and the tetratolyl compounds have high thermal stability. Thus, they do not decompose even when heated to 300-350°. Their decomposition with mercuric chloride (in acetone) with elimination of aryls in the form of the corresponding organomercury compound confirms the presence of four aryl groups in the substances obtained.

Potassium tetraphenylboron reacts in pyridine solution with the copper derivative of acetoacetic ester (when warmed for a few minutes), and yields a double compound of pyridine (pyridinate) with a copper tetraphenylboron containing a univalent copper atom.

$CuB(C_6H_5)_4 \cdot 4C_5H_5N$ is a light-yellow powder, which is converted by careful acidification into cuprous tetraphenylboron, a colorless substance of low stability.

The pyridinate of cuprous tetraphenylboron is comparatively stable: after being kept for several days, no signs of decomposition can be detected.

Under similar conditions (by the action of the copper derivative of acetoacetic ester on potassium tetra-p-tolylboron), we have prepared the pyridinate of copper tetra-p-tolylboron, which, unlike the phenyl compound, is very unstable. It crystallizes with three molecules of pyridine, and a few hours after its preparation an odor of pyridine appears and the substance darkens. Under the conditions described above it was not found possible to isolate copper tetratolylboron without combined pyridine: when an attempt was made to eliminate pyridine by means of dilute H_2SO_4, p,p'-bitolyl and metallic copper were obtained.

Potassium tetratolylboron reacts with bromine with formation mainly of bitolyl, which is an indication of the radical nature of the reaction, since an ionic mechanism would be expected to result in the formation of p-bromotoluene. Razuvaev and Brilkina [2] have shown that the compounds MBR_4 can undergo decomposition of the radical type; thus, agitation of $KB(C_6H_5)_4$ with mercury in chloroform for 70-80 hours resulted in the formation of diphenylmercury.

By no means all organomagnesium compounds react with potassium fluoborate to yield stable compounds of the type KBR_4. Thus, with methylmagnesium iodide and with p-methoxyphenylmagnesium bromide potassium fluoborate yields trimethylborine and tris-p-methoxyphenylborine, respectively. It may be supposed, however, that in these cases also compounds of the type KBR_4 are formed as intermediate compounds, but they are unstable and decompose. We carried out the reaction of methylmagnesium iodide with potassium fluoborate in ether in an atmosphere of nitrogen and then decomposed the reaction complex with water. Trimethylborine then separated and was identified in the form of its ammoniate. In the direct reaction between CH_3MgI and KBF_4, without addition of water, no trimethylborine separates – a fact that supports the idea of the intermediate formation of $KB(CH_3)_4$, decomposed by water with formation of $(CH_3)_3B$.

There are indications in the literature of the formation of tetraalkylboron salts. Schlesinger and Brown [3] have carried out the reaction between ethyllithium and trimethylborine, and they consider that they have obtained $Li[B(CH_3)_3C_2H_5]$, stable to dry air, but decomposed by water with evolution of gas. Somewhat later, lithium tetramethylboron was described [4]. The reaction between methylmagnesium iodide and potassium fluoborate provides a convenient method for the preparation of trimethylborine, since it makes it unnecessary to work with boron trifluoride.

It is interesting that triethyloxonium fluoborate reacts like potassium fluoborate with phenylmagnesium bromide:

$$(C_2H_5)_3O^+BF_4 + 4C_6H_5MgBr \rightarrow (C_2H_5)_3O^+B(C_6H_5)_4 + 4MgBrF.$$

The reaction proceeds with a yield of 30% of oxonium salt when an ether solution of the organomagnesium compound is added to triethyloxonium fluoborate. Triethyloxonium tetraphenylboron can be obtained in good yield also from $KB(C_6H_5)_4$ and $(C_2H_5)_3O^+BF_4$:

$$KB(C_6H_5)_4 + (C_2H_5)_3O^+BF_4 \rightarrow (C_2H_5)_3O^+B(C_6H_5)_4 + KBF_4.$$

Triethyloxonium tetraphenylboron is stable in the air, and is insoluble in water, but soluble in nitrobenzene; it melts at 115-116°. Like other oxonium salts it is an alkylating agent; thus it converts picric acid into ethyl picrate.

EXPERIMENTAL

Potassium Tetraphenylboron

To 4 g of KBF_4 80 ml of an ether solution of C_6H_5MgBr at a concentration of 0.27 g per ml was added. Reaction, accompanied by evolution of heat, began after a few minutes. The mixture was well-stirred, and reaction was complete in 2-3 hours. The mixture was poured into an ammonium chloride solution, and a precipitate separated that was insoluble both in water and in ether. It was filtered off, washed several times with water and ether, and dissolved in acetone. The acetone solution was filtered from unchanged KBF_4, and water was added. The precipitate that formed was filtered off and washed with water and ether. The yield of potassium tetraphenylboron was 8 g (70%).

Analysis for potassium was carried out as follows: to a weighed amount of the substance 25 ml of 0.1 N HCl and some ether were added (in absence of ether, dissolution is very slow), and when solution was complete the excess of HCl was titrated with alkali.

Found %: C 80.34; 80.51; H 5.64; 5.74; K 11.10
$C_{24}H_{20}BK$. Calculated %: C 80.44; H 5.60; K 10.91

The substance is soluble in cold acetone and in cold pyridine, but less soluble in hot acetone and in hot pyridine.

Potassium Tetra-p-tolylboron

Potassium fluoborate (1.44 g) was added to p-tolylmagnesium bromide prepared from 8 g of p-bromotoluene and 1.1 g of magnesium in 50 ml of ether. The reaction mixture was heated for three hours in a water bath with constant vigorous stirring, and was then poured into an ammonium chloride solution. At the interface between the aqueous and ethereal layers, a precipitate formed. The ether layer was separated together with the precipitate and was washed several times with water. The precipitate was filtered off, washed with ether, and dried, when 1.87 g of unpurified product was obtained. The potassium tetratolylboron was purified by dissolving it in acetone, filtering the turbid solution, and adding water. The resulting precipitate was filtered off and washed with water and ether. The yield was 32% on the amount of KBF_4 taken for reaction.

Found %: C 81.33; 81.39; H 7.26; 7.21; K 9.48

$C_{28}H_{28}BK$. Calculated %: C 81.16; H 6.81; K 9.41

Potassium tetratolylboron can be purified by adding cyclohexane to the acetone solution instead of water. Potassium tetratolylboron is insoluble in water and sparingly soluble in organic solvents.

Cuprous Tetraphenylboron

1) The copper derivative of acetoacetic ester (0.11 g) was added to 0.25 g of potassium tetraphenylboron in 10 ml of pyridine. The green solution was heated cautiously for a few minutes in a water bath until its color changed from green to dark brown. When the solution was cold, water was added, and the resulting precipitate was filtered off and washed with 1:1 aqueous pyridine and with water. The product was 0.23 g (96%) of the yellow pyridinate of cuprous tetraphenylboron.

Found %: C 75.63; H 5.86; N 8.04; 7.83

$C_{44}H_{40}N_4BCu$. Calculated %: C 75.68; H 5.77; N 8.04

2) Dilute sulfuric acid was added to an aqueous suspension of 0.22 g of $CuB(C_6H_5)_4 \cdot 4C_5H_5N$, and as the mixture was stirred the suspended solid turned from yellow to white. The cuprous tetraphenylboron was filtered off and washed with water. The yield was quantitative. The substance decomposed at 72-73°, and when exposed to the air it darkened fairly rapidly and an odor of biphenyl developed.

Found %: C 75.18; H 5.68

$C_{24}H_{20}BCu$. Calculated %: C 75.29; H 5.27

Cuprous Tetra-p-tolylboron

The copper derivative of acetoacetic ester (0.1 g) was added to 0.2 g of potassium tetra-p-tolylboron in 15 ml of pyridine. The mixture was carefully heated with constant agitation until the solution became clear and changed in color from green to dark brown, which required a few minutes. When the solution was cold, water was added, and the resulting precipitate was filtered off and washed with 1:1 aqueous pyridine, water, and low-boiling petroleum ether. The product was 0.12 g (67%) of $CuB(C_6H_4CH_3)_4 \cdot 3C_5H_5N$.

Found %: C 76.39; 76.48; H 6.26; 6.36; N 6.15

$C_{43}H_{43}N_3BCu$. Calculated %: C 76.38; H 6.41; N 6.22

The substance decomposed with storage. It was not found possible to isolate cuprous tetratolylboron without combined pyridine under the conditions of the previous experiment: p,p'-bitolyl and metallic copper were obtained.

Decomposition of Potassium Tetraphenylboron with Mercuric Chloride

To a solution of 0.1224 g of $KB(C_6H_5)_4$ in acetone, a little water was added, and then an acetone solution of 0.5 g of $HgCl_2$. There was an immediate precipitate of phenylmercury chloride. In order to complete the decomposition of the organoboron compound, the mixture was heated in a water bath, and the acetone was driven off. The phenylmercury chloride was filtered off and washed with water. The product was 0.41 g (95%) of C_6H_5HgCl, m.p. 252°. A mixture with authentic phenylmercury chloride melted at the same temperature.

Decomposition of Potassium Tetra-p-tolylboron with Mercuric Chloride

An acetone solution of 0.4 g (38% excess) of mercuric chloride was added to a solution of 0.1108 g of potassium tetra-p-tolylboron in acetone, and a few drops of water were added. The acetone was then slowly distilled off. When about one-quarter of the solvent remained in the flask, the condenser was set for reflux and the solution was heated for 30 minutes in a water bath. When the mixture was cool, water was added, and the precipitate of p-tolylmercury chloride was filtered off, washed with water, and dried. The product was 0.3166 g (94%) of p-tolylmercury chloride. It was recrystallized from benzene; m.p. 236-236.5°. A mixture with authentic p-tolylmercury chloride melted at 236-237°.

Action of Bromine on Potassium Tetra-p-tolylboron

A solution of dry bromine in chloroform was added to 1 g of potassium tetra-p-tolylboron in 10 ml of chloroform at room temperature with stirring until decolorization ceased to occur. Water was then added in order to dissolve the precipitated KBr. The chloroform layer was separated, washed with water, with 10% NaOH, and again with water, and then dried with $CaCl_2$. The chloroform was evaporated off, and the residue was recrystallized from alcohol, when 0.21 g (95%) of p,p'-bitolyl, m.p. 121°, was obtained. When this reaction was carried out in water — with bromine water under similar conditions — p,p'-bitolyl was again obtained, and in addition p-bromotoluene (identified in the form of p-toluic acid) was formed.

Action of Methylmagnesium Iodide on Potassium Fluoborate

Methylmagnesium iodide was prepared from 3 g of magnesium in 40 ml of absolute ether and 19 g of methyl iodide in 20 ml of ether in a flask fitted with a tube for the passage of nitrogen and a two-way adapter carrying a dropping funnel and a reflux condenser. The reaction was carried out in a current of pure dry nitrogen, and the apparatus was protected from access of moisture with the aid of a vessel containing sulfuric acid. When reaction was complete, the solution of methylmagnesium iodide was decanted in a current of nitrogen from the unchanged magnesium into a similar flask fitted with a tube for the passage of nitrogen, a dropping funnel, and a reflux condenser. Potassium fluoborate (3.4 g) was added; reaction began immediately, and the ether came to the boil. When reaction was complete, the sulfuric acid vessel was replaced by one containing strong aqueous ammonia cooled with ice. The reaction mixture was then decomposed by careful, dropwise addition of water from the dropping funnel. A liquid layer of the ammoniate of trimethylborine collected above the ammonia solution; it was separated from the aqueous layer and placed in a desiccator over sulfuric acid, where it solidified in the form of colorless crystals. The product was 1.23 g (62%) of trimethylborine ammoniate, m.p. 56°. The literature gives m.p. 56° [5, 6], but by the use of carefully purified trimethylborine and gaseous ammonia an ammoniate of m.p. 73.2-73.7° has been obtained [7].

Action of p-Methoxyphenylmagnesium Bromide on Potassium Fluoborate

Potassium fluoborate (1.44 g) was added to a solution of p-methoxyphenylmagnesium bromide prepared from 1.1 g of magnesium in 30 ml of absolute ether and 8.56 g of p-bromoanisole in 20 ml of absolute ether. The reaction mixture was heated in a water bath for three hours with constant vigorous stirring, after which it was poured into an ammonium chloride solution. The ether layer was separated and washed with water, and concentrated aqueous ammonia was then added. The mixture was shaken, and a precipitate formed at the interface between the aqueous and ethereal layers; it was filtered off and washed with water and ether. The product was 0.57 g (14%) of the ammoniate of tris-p-methoxyphenylborine, m.p. 185-189°; after recrystallization from alcohol it melted at 190°.

Found %: N 3.98
$C_{21}H_{24}O_3NB$. Calculated %: N 4.02

Triethyloxonium Tetraphenylboron

1. Double decomposition of potassium tetraphenylboron with triethyloxonium fluoborate. A freshly prepared solution of 1.3 g of $(C_2H_5)_3OBF_4$ [8] in acetone (when allowed to stand for a few minutes in acetone, triethyloxonium fluoborate decomposes) was added to 2.1 g of $KB(C_6H_5)_4$ dissolved in the least possible amount of acetone. A precipitate formed immediately and was rapidly filtered off (if it is left under acetone it decomposes); it was washed with a small amount of acetone. The product was 2-85 g of a mixture of $(C_2H_5)_3O^+B(C_6H_5)_4$ and KBF_4. In order to purify it from KBF_4 the substance was dissolved in nitrobenzene; the solution obtained was filtered, and precipitation with absolute ether yielded 1.8 g (73%) of triethyloxonium tetraphenylboron, m.p. 115-116°.

Found %: C 85.15; 85.01; H 8.44; 8.77
$C_{30}H_{35}OB$. Calculated %: C 85.29; H 8.35

2. Action of phenylmagnesium bromide on triethyloxonium fluoborate. An ether solution of C_6H_5MgBr (10 ml; concentration 0.394 g per ml) was added gradually to 1 g of $(C_2H_5)_3O^+BF_4$ in 15 ml of absolute ether; there was a vigorous reaction. The reaction mixture was stirred for a few minutes and poured into an ammonium chloride solution. The resulting precipitate, which was insoluble in water and in ether, was filtered off and washed with water and ether. It was dissolved for purification in nitrobenzene, the resulting solution was filtered, and the oxonium salt was precipitated with ether. The product was 0.67 g (30%) of triethyloxonium tetraphenylboron, m.p. 115-116°. In admixture with the preparation described in the previous experiment it showed no melting point depression.

3. Alkylation with triethyloxonium tetraphenylboron. Triethyloxonium tetraphenylboron (0.1 g) and picric acid (0.6 g) were heated with pure acetone until solution was complete. The reaction mixture was poured into water, and the ethyl picrate was extracted with ether, the extract being washed several times with water to remove picric acid. The ether was evaporated, and the residue was recrystallized from alcohol, and yielded 0.03 g of ethyl picrate, which melted after recrystallization from alcohol at 77-78°. A mixture with authentic ethyl picrate melted at the same temperature.

SUMMARY

1. A study has been made of the reaction of potassium fluoborate with organomagnesium compounds, namely phenylmagnesium, p-tolylmagnesium and p-methoxyphenylmagnesium bromides and methylmagnesium iodide. In the first two cases, the products were potassium tetraphenylboron and potassium tetra-p-tolylboron, respectively.

whereas p-methoxyphenylmagnesium bromide and methylmagnesium iodide yielded tris-p-methoxyphenylborine, and triphenylborine, respectively.

2. By reaction in pyridine of the copper derivative of acetoacetic ester with potassium tetraphenylboron and with potassium tetra-p-tolylboron the pyridinates of cuprous tetraphenylboron and cuprous tetra-p-tolylboron were obtained.

3. By reaction with phenylmagnesium bromide, and also with potassium tetraphenylboron, triethyloxonium fluoborate yields triethyloxonium tetraphenylboron.

Received February 1, 1954

M. V. Lomonosov Moscow State University

LITERATURE CITED

[1] G. Wittig, G. Keicher, A. Rückert, P. Raff, Ann., 563, 110 (1949); G. Wittig, P. Raff, Ann., 573, 195 (1951).

[2] G. A. Razuvaev and T. G. Brilkina, Proc. Acad. Sci. USSR, 85, No. 4, 815 (1952).

[3] H. I. Schlesinger, H. C. Brown, J. Am. Chem. Soc., 62, 3429 (1940).

[4] D. T. Hurd, J. org. Chem., 13, 711 (1948).

[5] E. Frankland, Ann., 124, 151 (1862).

[6] A. Stock, F. Zeidler, Ber., 54, 531 (1921).

[7] H. C. Brown, H. Bartholomay, Jr., M. D. Taylor, J. Am. Chem. Soc., 66, 435 (1944); H. C. Brown, J. Am. Chem. Soc., 67, 375 (1945).

[8] H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, G. Willfang, J. prak. Chem., 154, 111 (1939).

BLANK
PAGE

REACTIONS OF MERCAPTO AMINO ACIDS

COMMUNICATION 1. 3,3-DIMETHYLISOCYSTEINE AND ITS DERIVATIVES

I. L. Knunyants, M. G. Linkova, and P. G. Ignatenok

In recent years, owing to advances made in chemistry and biochemistry, the exceptional importance of sulfur-containing organic compounds in animal physiology is becoming more and more evident. The greatest significance is to be assigned to compounds containing the thiol group, particularly mercapto amino acids, which enter into the composition of a large number of specific proteins and enzymes. Thus, cysteine and glutathione retard the clotting of the blood and play a determining part in the regulation of certain oxidation-reduction processes. Methionine appears to be the only carrier of methyl groups for a series of compounds synthesized in the organism; its importance will be realized when it is remembered that it is an essential element in the diet of animals and is for that reason manufactured on the industrial scale.

Glutathione and cysteine, together with ascorbic acid, inhibit the activity of certain toxins (diphtherial); also they enter into the composition of insulin, and they have been applied with success in the treatment of certain forms of diabetes. It is probable that an essential part is played in the organism by other thiol compounds, such as coenzyme A, which is responsible for the acetylation of choline and phosphorylation of adenosine phosphates; it has been shown to contain 2-aminoethanethiol (decarboxylation product of cysteine), which in coenzyme A is attached by an amide linkage to pantothenic acid. The free thiol group of coenzyme A is the transmitter of the acetyl residue (via an ester of thiolacetic acid). Glutathione, which has a number of functions, plays a part also in the reduction of oxidized forms of coenzyme A.

The significance of the thiol group in the transfer of the acetyl group is evidenced in recently established facts relating to the extremely high acetylating power of thiolacetic acid, which acetylates various substances in the cold, including amino acids in aqueous solution at a pH of about 7. The special part played by thiol compounds can be seen also from the breakdown that occurs in physiological processes when substances capable of blocking thiol groups act upon the organism. Thus, the effects due to chloroarsines and lachrymatories are generally known, and these have now been shown to depend, according to the structure of the inhibitor, either on the alkylation or on the acylation of the thiol groups of enzymes. Blocking of the hexokinases of the skin results in serious skin affections, and so on.

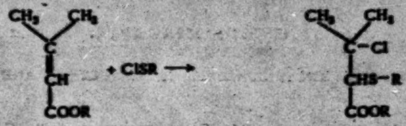
It is probable also that the antibiotic activity of many substances is associated with their ability to block the SH groups of the metabolites of bacteria. It has been found, for example, that penicillin has a high specificity in reactions with thiols. Other antibiotics containing double bonds conjugated with carbonyl are also able to combine with thiol-containing substances.

Penicillin, clavacin, streptomycin, bacitracin, and other antibiotics are inactivated by cysteine, glutathione, and BAL (2,3-dimercapto-1-propanol). The same occurs with unsaturated lactones, certain oxazolinones, and mixed anhydrides having antibiotic activity when they act selectively on certain thiol-containing compounds that are essential for cell metabolism. For this reason many mercapto amino acids and their derivatives have interesting physiological effects, and, although the mechanisms of these effects are not known in detail, it is clear that there are extensive opportunities for work in this field; particular interest is presented by those derivatives of mercapto amino acids that, owing to structural peculiarities, are reactive toward thiols.

Great interest is presented also by the elucidation of the biochemical role and action of those mercapto amino acids that are not indigenous to the organism and may be able to replace the metabolites. Thus, we have not yet determined the part played by dimethylcysteine, which can be obtained from penicillin and which, unlike other naturally occurring mercapto amino acids, is dextrorotatory. The action of the natural isomeric α-mercapto β-amino acids has not been elucidated at all; they have not been investigated owing to the fact that the only known member —isocysteine— has been obtained only in a minute amount by a complicated method.

In a series of investigations, the first of which is described in this paper, the authors have investigated a number of the reactions of β-mercapto α-amino acids and have effected the syntheses of some members of the isomeric series of α-mercapto β-amino acids.

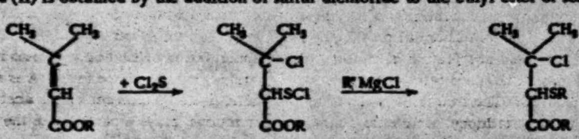
We have shown that alkanesulfenyl chlorides readily unite with unsaturated acids with formation of α-alkylthio β-chloro acids of the type:



(I)

In this way methane-, ethane-, α-toluene-, 2-chloroethane-, and 2-chloropropane-sulfenyl chlorides were caused to add to senecioic acid and its ethyl ester. The yields of the corresponding esters of 2-(alkylthio)-3-chloro-3-methylbutyric acids varied from 50% to 85%. In a number of cases, instead of the sulfenyl chlorides, the corresponding disulfides were taken for the reaction. In this variant of the method, a mixture of equimolecular amounts of the senecioic ester and the disulfide was treated with chlorine or sulfuryl chloride, when the nascent sulfenyl chloride formed immediately added at the double bond This method has an advantage in cases in which the sulfenyl chloride is unstable, as, for example, in the case of α-toluenesulfenyl chloride.

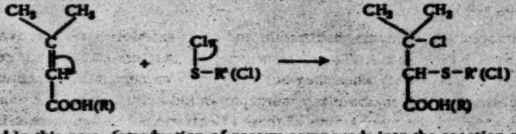
2-(Alkylthio)-3-chloro-3-methylbutyric acid and its derivatives can be obtained also from α-chlorothio β-chloro carboxylic acids by the action of alkylmagnesium halides. The ethyl ester of 3-chloro-2-(chlorothio)-3-methylbutyric acid (II) is obtained by the addition of sulfur dichloride to the ethyl ester of senecioic acid:



(II)

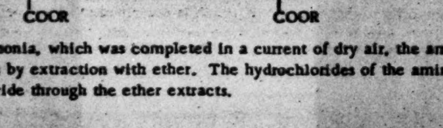
In this variant the fact that the reaction between sulfur dichloride and the unsaturated compound comes to a stop at the sulfenyl chloride stage is unprecedented: in all other cases, as is well-known, the reaction proceeds further and the corresponding sulfide is obtained. The resulting sulfenyl chloride (II) is stable, readily distils in a vacuum, and can be preserved for a long time without decomposition. The reaction of the sulfenyl chloride with benzylmagnesium chloride goes instantaneously and in quantitative yield. The resulting 2-(benzylthio)-3-chloro-3-methylbutytic ester is identical with the ester obtained by the reaction of dibenzyl disulfide with the ethyl ester of senecioic acid in presence of chlorine.

Thus, sulfur dichloride and alkanesulfenyl chlorides add to senecioic acid in the same direction, in accordance with the polarities of the original reactants:



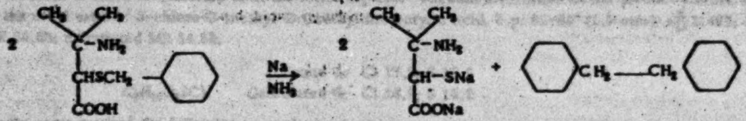
As would be expected in this case, introduction of peroxy compounds into the reaction medium does not affect the direction of the addition.

The resulting esters of 2-(alkylthio)-3-chloro-3-methylbutyric acids are readily converted into the corresponding esters of amino acids by keeping them for 10-12 hours in liquid ammonia in a closed vessel at room temperature:



After evaporation of the ammonia, which was completed in a current of dry air, the amino acid esters were separated from ammonium chloride by extraction with ether. The hydrochlorides of the amino acid esters were obtained by passage of hydrogen chloride through the ether extracts.

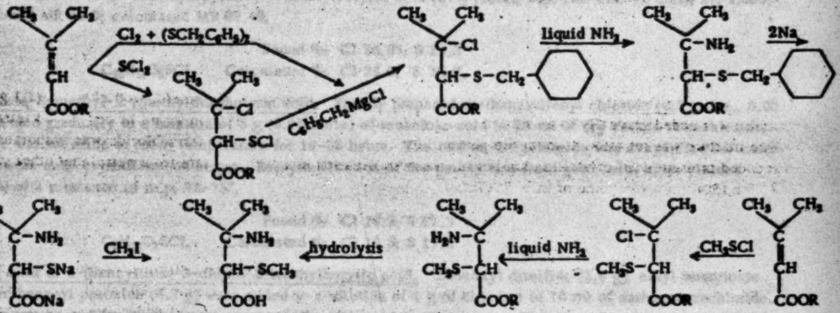
In no case was ammonolysis with formation of an amide observed, and the amino acid esters were obtained in 60-90% yield. The free amino acids were liberated by hydrolysis of the esters with 1:1 hydrochloric acid. S-Benzyl-3,3-dimethylisocysteine was debenzylated by means of sodium in liquid ammonia, and yielded the sodium salt of 3,3-dimethylisocysteine:



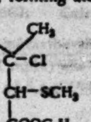
The direction of the addition of alkanesulfenyl chlorides and sulfur dichloride to senecioic acid and its ester was proved by comparison of the properties of the S-alkyl-3,3-dimethylisocysteines so obtained with those of the isomeric S-alkyl-3,3-dimethylcysteines synthesized by Savard [2] by the addition of thiols to 4-isopropylidene-2-phenyl-2-oxazolin-5-one.

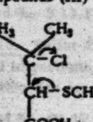
Treatment of S-benzyl-3,3-dimethylisocysteine with sodium in liquid ammonia, followed by methylation with methyl iodide, yielded S-methyl-3,3-dimethylisocysteine, identical with the S-methyl-3,3-dimethylisocysteine synthesized by the addition of methanesulfenyl chloride to the ethyl ester of senecioic acid.

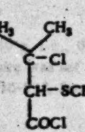
We give here a scheme illustrating the transformations effected:



In the course of our study of the addition products formed by sulfur chlorides with senecioic acid and its ester, a number of remarkable facts were noted. As already stated, methanesulfenyl chloride adds in similar fashion to senecioic acid and to its ester, forming the compounds (III) and (IV):


(IV)


(III)


(V)

The structure of the compound (IV) as a 3-chloro compound has been rigorously proved by us (above). The compound (III) is much less stable than (IV), and cannot be kept for a long time. When an attempt was made to esterify compound (III) with absolute alcohol in presence of hydrochloric acid, the ethyl ester of senecioic acid was obtained in quantitative yield. When it reacts with ammonia, (III) readily eliminates methanesulfenyl chloride and is converted into senecioic acid. The product of the addition of sulfur dichloride to senecioic acid behaves completely analogously: thus, when it is treated with ammonia, senecioic acid is readily regenerated.

On the basis of these transformations it might be concluded that (III) is a complex of methanesulfenyl chloride and senecioic acid. It is found, however, that when (III) is treated with thionyl chloride the acid chloride (V) of the corresponding acid is obtained, and this reacts normally with alcohol with formation of the ester (IV), which we obtained previously by the addition of methanesulfenyl chloride to the ester of senecioic acid. It is clear that 3-chloro-3-methyl-2-(methylthio)butyric acid is strongly polarized, as indicated in the structural formula (III).

EXPERIMENTAL

Ethyl ester of 3-chloro-3-methyl-2-(methylthio)butyric acid. Freshly prepared methanesulfenyl chloride (7.7 g) was added gradually to 9.3 g of the ethyl ester of senecioic acid ; the temperature rose to 40-45°. The mixture was set aside at room temperature until the following day. Vacuum distillation of the product yielded 16 g (70%) of the ethyl ester of 3-chloro-3-methyl-2-(methylthio)butyric acid, b.p. 81-83° (1.5 mm); n_D^{20} 1.491; d_4^{20} 1.118; found MR 54.53; calculated MR 54.84.

Found %: Cl 17.3; S 15.0
$C_8H_{15}O_2SCl$. Calculated %: Cl 16.9; S 15.2

By the same method the following were obtained:

ethyl ester of 3-chloro-2-(ethylthio)-3-methylbutyric acid (77% yield), b.p. 123-125° (15 mm).

Found %: Cl 15.5; S 15.6
$C_9H_{17}O_2SCl$. Calculated %: Cl 15.82; S 14.28;

ethyl ester of 3-chloro-2-(2-chloroethylthio)-3-methylbutyric acid (77% yield), b.p. 135-140° (17 mm),

Found %: Cl 26.82; S 12.74
$C_9H_{16}O_2SCl_2$. Calculated %: Cl 26.71; S 12.4;

ethyl ester of 3-chloro-2-(2-chloropropylthio)-3-methylbutyric acid (87% yield), b.p. 120-121° (1 mm); n_D^{20} 1.500; d_4^{20} 1.180; found MR 68.0; calculated MR 67.45,

Found %: Cl 26.57; S 14.3
$C_{10}H_{18}O_2SCl$. Calculated %: Cl 28.0; S 14.7.

3-Chloro-3-methyl-2-(methylthio)butyric acid. Freshly prepared methanesulfenyl chloride (4.1 g, i.e., 0.05 mole) was added gradually to a solution of 5 g (0.05 mole) of senecioic acid in 20 ml of dry carbon tetrachloride. The mixture was set aside at room temperature for 10-12 hours. The carbon tetrachloride was evaporated off under reduced pressure until crystallization began. Recrystallization of the precipitate from petroleum ether yielded 4.55 g (50%) of a substance of m.p. 73-75°.

Found %: Cl 19.2; S 17.3
$C_6H_{11}O_2SCl$. Calculated %: Cl 19.5; S 17.5

Ethyl ester of 2-(benzylthio)-3-chloro-3-methylbutyric acid. Dibenzyl disulfide (3.6 g), ethyl senecioate (3.83 g), and benzoyl peroxide (0.2 g) were added to a solution of 1 g of chlorine in 10 ml of carbon tetrachloride. The mixture was heated for two hours in a water bath. The solvent was driven off under reduced pressure, and the residue was distilled in a high vacuum. The product was 4.5 g (50%) of a substance of b.p. 134-136° (0.2 mm).

Found %: S 11.43; Cl 12.46
$C_{14}H_{19}O_2SCl$. Calculated %: S 11.17; Cl 12.39

3-Chloro-2-(chlorothio)-3-methylbutyric acid. Sulfur dichloride (30 g, i.e., 0.3 mole) was cooled to −5°, and senecioic acid (10 g, i.e., 0.1 mole) was added in portions. The mixture was set aside at room temperature until the next day. A precipitate of 5 g (25%) of yellowish crystals, m.p. 70-71°, formed.

Found %: Cl 35.4; S 16.0
$C_5H_8O_2Cl_2S$. Calculated %: Cl 35.0; S 15.7

Ethyl ester of 3-chloro-2-(chlorothio)-3-methylbutyric acid. Sulfur dichloride (15 g, i.e., 0.15 mole) was cooled to −5° and was stirred while gradual addition was made of 6.4 g (0.05 mole) of ethyl senecioate over a period of 15-20 minutes. The resulting mixture was set aside at room temperature until the next day. The excess of sulfur dichloride was driven off under reduced pressure from a water bath, and the residue was vacuum-distilled, when it yielded 10 g (87%) of the ethyl ether of 3-chloro-2-(chlorothio)-3-methylbutyric acid, b.p. 95-98° (1-2 mm), in the form of a mobile orange liquid of characteristic odor.

Found %: Cl 31.1; S 13.93; Cl 15.1 (iodometrically)
$C_7H_{12}O_2Cl_2S$. Calculated %: Cl 30.73; S 13.85; Cl 15.36

Ethyl ester of 2-(benzylthio)-3-chloro-3-methylbutyric acid. A solution of 5.8 g of the ethyl ester of 3-chloro-2-(chlorothio)-3-methylbutyric acid in 100 ml of absolute ether was cooled with ice water, and benzylmagnesium chloride (0.7 g Mg, 200 ml of absolute ether, 3.6 g of benzyl chloride) was added from a dropping funnel to the stirred solution. A white precipitate of magnesium chloride formed. When the addition was complete, the mixture was allowed to stand for 30 minutes at room temperature; it was then washed free from $MgCl_2$ with water in a separating funnel. The ether solution was dried over calcium chloride, and the ether was driven off. Vacuum distillation of the residue yielded 4 g (60.4%) of product, b.p. 134-136° (0.2 mm).

Reduction of the ethyl ester of 3-chloro-2-(chlorothio)-3-butyric acid. The ethyl ester of 3-chloro-2-(chlorothio)-3-butyric acid (5 g) was dissolved in 250 ml of ether. The solution was transferred to a separating funnel, and 100 ml of acidified 5% potassium iodide solution was added in portions and the mixture shaken. As reaction proceeded, a considerable amount of iodine separated and the temperature rose appreciably; reaction was complete in 10-15 minutes. The iodine was removed by washing the mixture with a thiosulfate solution. The ether layer was separated and dried over calcium chloride; the ether was driven off under reduced pressure, and the residue was distilled in a high vacumm, when a quantitative yield (4 g) of the diethyl ester of 2,2'-dithiobis[3-chloro-3-methylbutyric acid], b.p. 173-175° (0.2 mm) was obtained.

Found %: Cl 18.6; S 16.7

$C_{14}H_{24}O_4Cl_2S_2$. Calculated %: Cl 18.18; S 16.3

Hydrochloride of the ethyl ester of S,3,3-trimethylisocysteine. The ethyl ester of 3-chloro-3-methyl-2-(methylthio)butyric acid (9 g) was introduced into 50 ml of liquid ammonia. The autoclave was closed, and the reaction mixture was allowed to stand until the next day at room temperature. The ammonia was allowed to evaporate off, and the residue was extracted with ether. The ether extract was washed with water and dried over potassium carbonate. Dry HCl was passed until an acid reaction to Congo red was obtained. A precipitate of the hydrochloride of the ethyl ester of S,3,3-trimethylisocysteine formed; it was dissolved for purification in a small amount of absolute alcohol, and absolute ether was added until a slight turbidity appeared. By the next day 7.7 g (80%) of a crystalline product, m.p. 118-120°, had formed.

Found %: Cl 15.8; S 13.8; N 6.11

$C_8H_{17}O_2NSCl$. Calculated %: Cl 15.6; S 14.0; N 6.16

By the same method the following were obtained:

hydrochloride of the ethyl ester of S-ethyl-3,3-dimethylisocysteine (67% yield), m.p. 70-71°,

Found %: Cl 14.1; N 6.0

$C_9H_{19}O_2NS \cdot HCl$. Calculated %: Cl 14.7; N 5.8;

hydrochloride of the ethyl ester of S-benzyl-3,3-dimethylisocysteine (60.7% yield), m.p. 167-168°,

Found %: Cl 11.9; N 4.5

$C_{14}H_{21}O_2NS \cdot HCl$. Calculated %: Cl 11.7; N 4.6;

hydrochloride of the ethyl ester of S-2-chloroethyl-3,3-dimethylisocysteine (60.5% yield), m.p. 115-116°,

Found %: Cl 12.71 (Volhard)

$C_9H_{18}O_2NSCl \cdot HCl$. Calculated %: Cl 13.08;

hydrochloride of the ethyl ester of S-2-chloropropyl-3,3-dimethylisocysteine (65.5% yield), m.p. 147-148°,

Found %: N 4.7; Cl 11.8 (Volhard)

$C_{10}H_{20}O_2NSCl \cdot HCl$. Calculated %: N 4.82; Cl 12.2

S-Benzyl-3,3-dimethylisocysteine. A mixture of 7.2 g (0.002 mole) of the hydrochloride of the ethyl ester of S-benzyl-3,3-dimethylisocysteine and 60 ml of diluted HCl (one part of acid sp.gr. 1.19 and one part of water) was heated over a gauze for four hours under reflux. The solution was filtered and evaporated to dryness on a water bath. The residue was dissolved in 20 ml of water and neutralized with bicarbonate to pH 5, when the free S-benzyl-3,3-dimethylisocysteine came down (m.p. 189-190° with decomposition). Recrystallization from water yielded 5 g (86%) of product, m.p. 192-193°. A mixture with S-benzyldimethylcysteine prepared by Savard's method melted at 175-176° with decomposition (14° depression).

Found %: N 6.1

$C_{12}H_{17}O_2NS$, Calculated %: N 5.9

S-Ethyl-3,3-dimethylisocysteine was obtained in 49% yield; m.p. 202-203°.

Found %: N 7.9

$C_7H_{15}O_2NS$, Calculated %: N 7.9

S,3,3-Trimethylisocysteine. a) A solution of 2.5 g of the hydrochloride of the ethyl ester of S,3,3-trimethylisocysteine in 1:1 hydrochloric acid was boiled for two hours under reflux. The solution was then evaporated to dryness, dissolved in 7 ml of water, and neutralized with bicarbonate to pH 5.6. The precipitate that formed was pressed off. Crystallization from water yielded 1 g (62.5%) of a substance of m.p. 210-212°.

Found %: N 8.52; S 19.5
$C_6H_{13}O_2NS$. Calculated %: N 8.58; S 19.7

b) S-Benzyl-3,3-dimethylisocysteine (2 g) was dissolved in 100 ml of liquid ammonia. The solution was stirred and 0.5 g of sodium was added in small portions. A blue coloration of the solution, permanent over ten minutes, indicated the end of the reaction. The excess of sodium was removed by addition of ammonium chloride (decolorization). Methyl iodide (1.2 g) was then added, and the mixture was set aside until the next day. The ammonia was removed, and the residue was dissolved in 7 ml of water. The bibenzyl was repeatedly extracted with ether, and the aqueous solution was acidified to pH 5.6. The precipitate was filtered off and recrystallized from water, when 0.5 g of a substance of m.p. 211-212° was obtained.

Hydrochloride of 3,3-dimethylisocysteine. The elimination of the benzyl group from S-benzyl-3,3-dimethylisocysteine was carried out as in the preceding experiments, the same quantities being used. To the aqueous solution obtained (10 ml), 100 ml of a saturated solution of mercuric chloride was added, and the mixture was shaken for one hour. The precipitated mercury derivative rapidly coagulated. The mixture was set aside until the next day, when the precipitate was pressed off, washed with water, and dissolved in 5 ml of 10% HCl. The solution was filtered, and mercury was precipitated with hydrogen sulfide. The solution was filtered and evaporated down, first under reduced pressure at room temperature, and then in a vacuum desiccator over NaOH. The resulting crystalline precipitate was very hygroscopic.

Found %: N 7.27
$C_5H_{12}O_2NSCl$. Calculated %: N 7.54

Acid chloride of 3-chloro-3-methyl-2-(methylthio)butyric acid. Thionyl chloride (11 g) was added to a solution of 7.5 g of 3-chloro-3-methyl-2-(methylthio)butyric acid in 40 ml of dry carbon tetrachloride, and the mixture was heated until the evolution of HCl and SO_2 ceased. The carbon tetrachloride was driven off, and the residue was fractionated, when it yielded 8.4 g (60%) of the acid chloride of 3-chloro-3-methyl-2-(methylthio)butyric acid, b.p. 71-72° (3 mm); n_D^{20} 1.514; d_4^{20} 1.225; found MR 48.57; calculated MR 47.93.

Found %: Cl 34.6; S 15.4
$C_6H_{10}OSCl_2$. Calculated %: Cl 35.3; S 15.9

Ethyl ester of 3-chloro-3-methyl-2-(methylthio)butyric acid. Absolute alcohol (5 ml) was added dropwise to 8.4 g of the acid chloride of 3-chloro-3-methyl-2-(methylthio)butyric acid; reaction occurred with evolution of heat. When the evolution of HCl ceased, the mixture was vacuum-fractionated, and yielded 5.6 g (67%) of a substance of b.p. 81-83° (1.5 mm). The ethyl ester of 3-chloro-3-methyl-2-(methylthio)butyric acid so prepared was identical in properties with the ester prepared by another method (see the first experiment).

Reaction of 3-chloro-3-methyl-2-(methylthio)butyric acid with ammonia. 3-Chloro-3-methyl-2-(methylthio)butyric acid (1.5 g) was introduced into 50 ml of liquid ammonia. The autoclave was closed and left for twelve hours at room temperature. The ammonia was evaporated off, and the residue was dissolved in 5 ml of water. The solution was acidified with hydrochloric acid, and the resulting precipitate was pressed off and washed with water. The product (0.4 g) melted at 63-65°, undepressed by admixture with senecioic acid.

Reaction of 3-chloro-3-methyl-2-(methylthio)butyric acid with ethanol. A solution of 3.6 g of 3-chloro-3-methyl-2-(methylthio)butyric acid in 20 ml of absolute ethanol was saturated with dry hydrogen chloride, and the mixture was set aside for twelve hours at room temperature. Fractionation yielded ethyl senecioate, b.p. 36-38° (15 mm).

SUMMARY

1. The addition reactions of sulfur dichloride and alkanesulfenyl chlorides with senecioic acid and its ethyl ester have been described.

2. It has been shown that, unlike the addition of sulfur dichloride to olefins (which leads to the formation of symmetrical sulfides), its addition to senecioic acid and its ethyl ester yields stable sulfenyl chlorides.

3. By treatment of the addition products with ammonia, 3,3-dimethylisocysteine (isomer of the naturally occurring 3,3-dimethylcysteine) and a number of its derivatives have been synthesized.

Received April 9, 1954 N. D. Zelinsky Institute of Organic Chemistry of the USSR Academy of Sciences

LITERATURE CITED

[1] Gabriel, Ber., 38, 630 (1905).

[2] K. Savard, et. al., J. Can. Res., 24, No. 1, 28 (1946).

REACTIONS OF MERCAPTO AMINO ACIDS

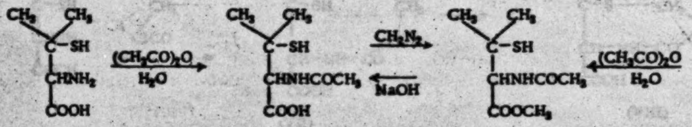
COMMUNICATION 2. ACYLATION AND ALKYLATION OF 3,3-DIMETHYLCYSTEINE

I. L. Knunyants and M. G. Linkova

3,3-Dimethylcysteine and its esters are readily acylated in an aqueous medium in presence of alkali. However, there is no proof that in all of these cases it is the amino group that is acylated; on the contrary, in view of the absence of reactions for the thiol group in acyl derivatives of 3,3-dimethylcysteine esters, the opposite conclusion might very well be reached.

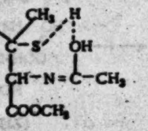
Acetylation of 3,3-dimethylcysteine with acetic anhydride or acetyl chloride yields an acetyl-3,3-dimethylcysteine of m.p. 182-183° (I) which gives a positive reaction for the thiol group. When an ester of 3,3-dimethylcysteine is acetylated, either with acetyl chloride in absolute ether or with acetic anhydride in water, in both cases the same acetyl derivative (II) of the ester is obtained, and this does not give a positive reaction with ferric chloride or sodium nitroprusside.

In order to determine the structures of these substances, the acetyl derivative of 3,3-dimethylcysteine was converted into its methyl ester by the action of diazomethane, and this was found to be identical with the product of the acetylation of the methyl ester of 3,3-dimethylcysteine:



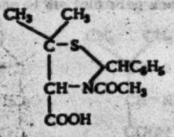
(I) (II)

Hydrolysis of this ester yielded the acetyl-3,3-dimethylcysteine of m.p. 182-183°. A mixture test with the product obtained by the acetylation of free 3,3-dimethylcysteine showed no depression. It was thus established that the acylation not only of 3,3-dimethylcysteine itself, but also of its esters occurs at a nitrogen atom. Absence of a reaction for the thiol group in esters of N-acyl derivatives of dimethylcysteine may arise from the formation of a strong intramolecular hydrogen bond (III):



(III)

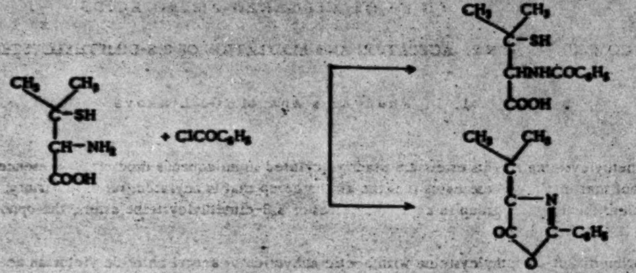
It is noteworthy that N-acetyl-3,3-dimethylcysteine reacts readily with benzaldehyde with formation of 3-acetyl-5,5-dimethyl-2-phenyl-4-thiazolinecarboxylic acid (IV) (m.p. 172-173° with decomposition):



(IV)

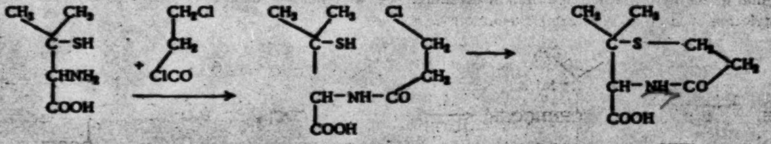
whereas it is known that N-acyl derivatives of amines generally do not react with aldehydes [1].

The benzoylation of 3,3-dimethylcysteine proceeds in a peculiar fashion: when the dimethylcysteine is treated with benzoyl chloride under Schotten-Baumann conditions, not only N-benzoyl-3,3-dimethylcysteine, but also 4-isopropylidene-2-phenyl-2-oxazolin-5-one (VI) is obtained in considerable amount:


(V)

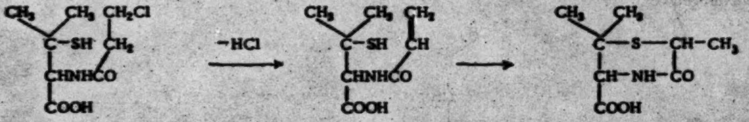
(VI)

Phenylacetyl chloride reacts normally with 3,3-dimethylcysteine with formation of N-(phenylacetyl)-3,3-dimethylcysteine, m.p. 130-131°. 3,3-Dimethylcysteine and its ester reactiwith 3-chloropropionyl chloride with formation in high yield of N-(3-chloropropionyl)-3,3-dimethylcysteine (VII) and its ester respectively. When N-(3-chloropropionyl)-3,3-dimethylcysteine is treated with aqueous or alcoholic alkali, it is converted smoothly into the compound (VIII):


(VII)

(VIII)

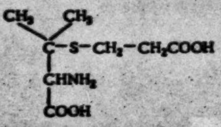
The structure (VIII), which contains a seven-membered ring, is open to some doubt, however, for apart from the alkylation reaction between the thiol group and the 3-chloropropionyl residue in (VII) with formation of (VIII), another possible reaction is not excluded, namely, the elimination of hydrogen chloride from the N-β-chloropropionyl)-3,3-dimethylcysteine with formation of the intermediate compound (IX), and the subsequent addition of the thiol group with formation of the compound (X) containing a six-membered ring:

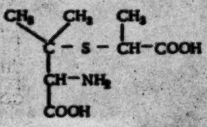


(IX)

(X)

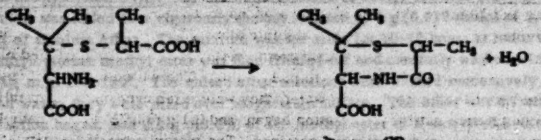
The question was resolved by a comparison of the hydrolysis products of (VIII) with synthetic amino acids obtained by the alkylation of 3,3-dimethylcysteine with 3-iodopropionic and 2-bromopropionic acids. Hydrolysis of (VIII) with a mixture of formic and hydrochloric acids yielded an amino acid, which, in correspondence with the structure (VIII) or the structure (X) could have one of the following structures:


(XI)


(XII)

The syntheses of these amino acids could be effected by determining the conditions for the S-alkylation of 3,3-dimethylcysteine. Experiment showed that 3,3-dimethylcysteine readily reacts with alkyl halides in an aqueous medium at pH 8-9 with formation of S-alkyl derivatives. Thus, with methyl iodide and benzyl chloride quantitative yields were obtained of S-methyl- and S-benzyl-3,3-dimethylcysteine, which were found to be identical with the substances obtained by Savard and coworkers [2] by the alkylation of 3,3-dimethylcysteine with methyl iodide in liquid ammonia and the addition of α-toluenethiol to 4-isopropylidene-2-phenyl-2-oxazolin-5-one.

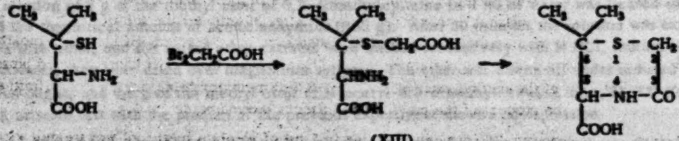
The extension of these reactions to 3-iodopropionic and 2-bromopropionic acids resulted in the preparation of two different amino acids, of which the product of the alkylation of 3,3-dimethylcysteine with 3-iodopropionic acid (S-(2-carboxyethyl)-3,3-dimethylcysteine) (XI) was found to be identical with the amino acid obtained from (VIII). The acid obtained from 3,3-dimethylcysteine and 2-bromopropionic acid was found to be widely different in its properties: it could be obtained only in the form of its hydrochloride. When an attempt was made to obtain the acid (XII) in the free state, elimination of water unexpectedly occurred with ring closure, yielding the compound (X) containing a six-membered ring:



(X)

It was thus shown that the condensation product formed by 3,3-dimethylcysteine with 3-chloropropionyl chloride contains a seven-membered ring.

Unusually facile cyclization was observed also in the alkylation of 3,3-dimethylcysteine with bromoacetic acid, the product being 2,2-dimethyl-5-oxo-3-thiamorpholinecarboxylic acid (XIV):



(XIII)

(XIV)

The 2,2-dimethyl-5-oxo-3-thiamorpholinecarboxylic acid so obtained was found to be identical with the previously obtained [3] product of the condensation of 3,3-dimethylcysteine with chloroacetyl chloride. Unlike S-(carboxymethyl)-3,3-dimethylcysteine (XIII), S-(2-carboxyethyl)-3,3-dimethylcysteine (XI) does not undergo cyclization under these conditions.

EXPERIMENTAL

N-Acetyl-3,3-dimethylcysteine (I). a) Sodium acetate (7 g) was added to a solution of 10 g of the hydrobromide of 3,3-dimethylcysteine in 25 ml of water, and after 10-15 minutes the mixture was shaken vigorously while 5.0 g (20% excess) of acetic anhydride was added. Reaction occurred with evolution of heat, and a precipitate of N-acetyl-3,3-dimethylcysteine appeared already during the first hour. The reaction mixture was set aside at room temperature overnight. On the next day the precipitate was filtered off, washed twice with small amounts of water and with alcohol, and dried in an vacuum desiccator over P_2O_5. The product was 5 g (55%) of N-acetyl-3,3-dimethylcysteine, m.p. 182-183° with decomposition. After recrystallization the melting point was 186-187°. N-Acetyl-3,3-dimethylcysteine is insoluble in ether, difficultly soluble in cold water, and readily soluble in alcohol and in hot water.

Found %: N 7.32

$C_7H_{13}O_3NS$. Calculated %: N 7.32

b) The methyl ester of N-acetyl-3,3-dimethylcysteine (0.1 g) was dissolved in the equivalent amount of 2 N aqueous NaOH. The solution was heated at 50° for 30 minutes, and was then cooled and neutralized with 2 N HCl. The resulting precipitate was filtered off, washed with water, and dried in a vacuum desiccator over P_2O_5. The product was 50 mg of N-acetyl-3,3-dimethylcysteine, m.p. 182-183°. A mixture test with the substance obtained by the acetylation of 3,3-dimethylcysteine with acetic anhydride showed no depression.

Methyl ester of 3,3-dimethylcysteine. A solution of 13 g (0.1 mole) of the hydrobromide of 3,3-dimethylcysteine in ten times the amount of absolute methanol was saturated with dry hydrogen chloride and left at room temperature for 10-12 hours. The mixture was then heated for 4-5 hours in a water bath, and the alcohol was driven off at 40-50° under reduced pressure. A solution of the residue in dry chloroform was cooled to 0°, and dry ammonia was passed until the mixture was alkaline to phenolphthalein. The resulting precipitate was filtered off and washed several times with chloroform. The united chloroform washings were evaporated down under reduced pressure, and the residue was vacuum-fractionated, yielding 5 g (60%) of the methyl ester of 3,3-dimethylcysteine, b.p. 78° (1 mm). The hydrochloride of 3,3-dimethylcysteine methyl ester melts at 184-185° with decomposition. The methyl ester of 3,3-dimethylcysteine is a colorless glycerollike liquid having a pleasant odor. It is readily soluble in water, alcohol, and ether; n_D^{20} 1.4850; d_4^{20} 1.105; found MR 42.35; calculated for $C_6H_{13}O_2NS$ MR 42.65.

Methyl ester of N-acetyl-3,3-dimethylcysteine (II). a) An ether solution of acetyl chloride (0.97 g, i.e., 0.006 mole, and 10 ml of absolute ether) was added to a vigorously shaken solution of 4 g (0.012 mole) of 3,3-dimethylcysteine methyl ester in 15 ml of absolute ether. The mixture was set aside for 10-12 hours at room temperature. The hydrochloride of 3,3-dimethylcysteine methyl ester was then filtered off and carefully washed with absolute ether; the yield was 2.3 g (94.2%); m.p. 175-180°. The united ether solutions were washed successively with N HCl, sodium bicarbonate solution, and water; they were dried over magnesium sulfate. The ether was driven off under reduced pressure until crystallization began, and 2.1 g (83.6%) of the methyl ester of N-acetyl-3,3-dimethylcysteine, m.p. 80-82° (from ether), was obtained. The methyl ester of N-acetyl-3,3-dimethylcysteine is soluble in water and very soluble in alcohol, ether, and acetone. Reactions for the thiol group with $FeCl_3$ and with sodium nitroprusside were negative; reactions with iodine and with lead acetate were positive.

	Found %:	C 46.77; H 7.43; N 6.86
$C_8H_{15}O_3NS$.	Calculated %:	C 46.83; H 7.3; N 6.83

b) A solution of 1 g of the methyl ester of 3,3-dimethylcysteine in 3 ml of water was treated under vigorous shaking with the theoretical amount of acetic anhydride (0.62 g). After 30 minutes the solution was extracted several times with ether, and the united ether extracts were washed successively with N HCl, sodium bicarbonate solution, and water; they were dried over magnesium sulfate. The ether was driven off under reduced pressure until crystallization began, and 0.8 g of the methyl ester of N-acetyl-3,3-dimethylcysteine, m.p. 81-83° (from ether), was obtained. A mixture test with the product of the previous experiment showed no depression.

c) A solution of 1 g of N-acetyl-3,3-dimethylcysteine in 2 ml of absolute methanol was treated with an ethereal solution of diazomethane. After 30 minutes the alcohol and ether were evaporated away under reduced pressure, and the residue was dissolved in ether. The ether solution was washed successively with sodium bicarbonate solution and with water; it was dried over magnesium sulfate. After evaporation of the solution under reduced pressure, the residue was recrystallized from a small amount of ether. A substance of m.p. 80-82°, identical with that described above, was obtained.

	Found %:	N 6.76
$C_8H_{15}O_3NS$.	Calculated %:	N 6.83

3-Acetyl-5,5-dimethyl-2-phenyl-4-thiazolidinecarboxylic acid (IV). N-Acetyl-3,3-dimethylcysteine (1 g) was mixed with 1.1 g (100% excess) of benzaldehyde, and 2 ml of dioxane saturated with dry HCl was added. Reaction occurred with appreciable evolution of heat; the whole went into solution, but after 10-15 minutes a new precipitate formed. On the next day the precipitate was filtered off and washed with dry ether. The product was 1.17 g (80%) of 3-acetyl-5,5-dimethyl-2-phenyl-4-thiazolidinecarboxylic acid, m.p. 172-175° with decomposition (from alcohol). The substance is readily soluble in alcohol, dioxane and hot water, but almost insoluble in ether.

	Found %:	C 59.07; H 6.25; N 5.09
$C_{14}H_{17}O_3NS$.	Calculated %:	C 60.2; H 6.1; N 5.02

Benzoylation of 3,3-dimethylcysteine (to give (V) and (VI)). Sodium bicarbonate (1.7 g) was added to a solution of 3 g (0.02 mole) of 3,3-dimethylcysteine in 10 ml of water, and then, at 0°, 2.8 g (0.02 mole) of benzoyl chloride and 1.7 g of sodium bicarbonate were added successively. After a short time there formed a crystalline precipitate of 4-isopropylidene-2-phenyl-2-oxazolin-5-one (VI) (1.5 g), m.p. 96-97° (from alcohol). A mixture test with an authentic sample showed no melting point depression. The filtrate was acidified with N HCl to Congo red. N-Benzoyl-3,3-dimethylcysteine (V) came down as an oil, which slowly solidified. The yield of (V) was 2 g (30%); m.p. 138-140° (from benzene). For the melting point, the literature gives 135-136°.

N-Phenylacetyl-3,3-dimethylcysteine. A solution of 1.49 g (0.01 mole) of 3,3-dimethylcysteine and 2.86 g of $Na_2CO_3 \cdot 10H_2O$ in 8 ml of water was cooled to −5° and was stirred while 1.5 g (0.01 mole) of phenylacetyl chloride was added. After two hours the temperature was brought to that of the room, 20 ml of ether was added, and the mixture was acidified to Congo Red with 2N HCl. The ether solution was separated, and the aqueous layer was extracted twice with ether. The united ether extracts were dried over magnesium sulfate and evaporated under reduced pressure until crystallization began. The product was 0.9 g (34%) of N-phenylacetyl-3,3-dimethylcysteine, m.p. 130-131°.

Found %: C 58.39; H 6.56; N 5.28

$C_{13}H_{17}O_3NS$. Calculated %: C 58.42; H 6.36; N 5.23

Methyl ester of N-(3-chloropropionyl)-3,3-dimethylcysteine. An ether solution of 1.7 g (0.01 mole) of 3-chloropropionyl chloride was added gradually at room temperature to a solution of 3.2 g (0.02 mole) of the methyl ester of 3,3-dimethylcysteine in 100 ml of absolute ether. The mixture was set aside until the next day. The precipitate of the hydrochloride of the 3,3-dimethylcysteine ester was filtered off and carefully washed on the filter with absolute ether. The united ether solutions were washed successively with 0.1 N HCl and water. They were dried over magnesium sulfate and evaporated under reduced pressure until crystallization began. The yield of the methyl ester of N-(3-chloropropionyl)-3,3-dimethylcysteine was 1.7 g (68%); m.p. 61-62°.

Found %: C 42.9 H 6.5; N 5.56

$C_9H_{16}O_3NSCl$. Calculated %: C 42.5; H 6.3; N 5.5

Hexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid (VIII). The methyl ester of N-(3-chloropropionyl)-3,3-dimethylcysteine (0.25 g, i.e., 0.001 mole) was dissolved in methanol (5 ml), and 0.5 N $Ba(OH)_2$ (4 ml) was added. The mixture was set aside at room temperature until the next day, and was then acidified to Congo Red with N HCl. The precipitate was filtered off, redissolved in sodium bicarbonate solution, and again precipitated with N HCl. The yield of hexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid was 0.15 g; m.p. 266-270°.

Found %: C 46.04; H 6.7; N 6.87

$C_8H_{13}O_3NS$. Calculated %: C 47.2; H 6.3; N 6.9

N-(3-Chloropropionyl)-3,3-dimethylcysteine (VII). A solution of 0.9 g of 3,3-dimethylcysteine and 1 g of sodium bicarbonate in 10 ml of water was cooled to 0°, and 0.8 g of 3-chloropropionyl chloride was added gradually. After two hours the temperature was brought to that of the room, and the mixture was filtered and acidified to Congo Red with N HCl. The precipitate was filtered off, and recrystallization from water yielded 0.6 g (50%) of N-(3-chloropropionyl)-3,3-dimethylcysteine, m.p. 155-156°. When treated with two molecular proportions of NaOH, N-(3-chloropropionyl)-3,3-dimethylcysteine yielded the compound (VIII), m.p. 269-273°, described above; there was no depression in a mixture melting point test.

Hydrolysis of hexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid. Hexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid (1 g) was heated for two hours under reflux with 30 ml of a mixture of equal volumes of formic acid, hydrochloric acid, and water. The solution was filtered and evaporated to dryness under reduced pressure. The residue was dissolved in 10 ml of absolute alcohol, and 1 ml of pyridine was added. The precipitate was filtered off and washed with absolute alcohol. The product was 0.4 g of S-(2-carboxyethyl)-3,3-dimethylcysteine, m.p. 181-182°.

Found %: C 44.02; H 6.89; S 14.8; N 6.6

$C_8H_{15}O_4NS$. Calculated %: C 43.4; H 6.7; S 14.5; N 6.33

S,3,3-Trimethylcysteine. A solution of 0.15 g (0.001 mole) of 3,3-dimethylcysteine in 5 ml of water was brought to pH 8 with N NaOH, 0.15 g (0.001 mole) of methyl iodide was added, and the mixture was shaken. After 30 minutes the reaction for the thiol group was negative. The solution was acidified to pH 5.8-6 with N HCl. The precipitated S,3,3-trimethylcysteine was pressed off and recrystallized from water; m.p. 253-254° (the literature gives 254-256°). The yield was almost quantitative.

S-Benzyl-3,3-dimethylcysteine. A solution of 0.3 g (0.002 mole) of 3,3-dimethylcysteine in 6 ml of water was brought to pH 9 with N NaOH, 0.25 g (0.002 mole) of benzyl chloride was added, and the mixture was shaken at 40°. After one hour the solution was cooled and acidified to pH 5.8-6 with N HCl. The precipitated S-benzyl-3,3-dimethylcysteine was pressed off and recrystallized from water; m.p. 182-183°. A mixture test with the S-benzyl-3,3-dimethylcysteine obtained by Savard's method showed no depression.

S-(2-Carboxyethyl)-3,3-dimethylcysteine (XI). 3,3-Dimethylcysteine (0.15 g, i.e., 0.001 mole) was dissolved in 3 ml of water, and 0.2 g (0.001 mole) of 3-iodopropionic acid and 3 ml of N NaOH were added. After one hour the solution was acidified to Congo Red with N HCl and evaporated down under reduced pressure. The dry residue was dissolved in absolute ethanol and the solution filtered; 0.2 ml of pyridine was added to remove HCl.

The precipitated S-(2-carboxyethyl)-3,3-dimethylcysteine was pressed off and washed with absolute alcohol. The yield was 0.17 g (84.5%); m.p. 181-183°, undepressed by admixture of S-(2-carboxyethyl)-3,3-dimethylcysteine obtained by the hydrolysis of (VIII).

2,2,6-Trimethyl-5-oxo-3-thiamorpholinecarboxylic acid (X). a) 3,3-Dimethylcysteine (0.32 g, i.e., 0.002 mole) was dissolved in 5 ml of water, and 6.6 ml of N NaOH and 0.3 g of 2-bromopropionic acid were added. After four hours the solution was acidified to Congo Red with N HCl and evaporated to dryness under reduced pressure. The residue was dissolved in absolute ethanol and the solution filtered; 0.5 ml of pyridine was added, and the mixture was set aside for twelve hours. On the next day the alcohol was evaporated off, 5 ml of water was added, and the solution was filtered. After recrystallization from water the melting point of the substance (X) was 188-189°.

Found %: C 46.3; H 6.7; S 15.6; N 7.11
$C_8H_{13}O_3NS$. Calculated %: C 47.2; H 6.4; S 15.7; N 6.9

b) The substance (X) was obtained also by the acylation of 3,3-dimethylcysteine with 2-bromopropionyl bromide by the Schotten-Baumann method.

Hydrochloride of S-(1-carboxyethyl)3,3-dimethylcysteine (XII). A mixture of 0.1 g of 2,2,6-trimethyl-5-oxo-3-thiamorpholinecarboxylic acid (X) and 2 ml of 15% HCl was heated for two hours under reflux. The solution was then evaporated to dryness under reduced pressure. The residue was dissolved in absolute alcohol, and five times the volume of absolute ether was added, when a precipitate formed of the hydrochloride of S-(1-carboxyethyl)-3,3-dimethylcysteine (XII), m.p. 172-174° with decomposition (in a closed capillary).

Found %: C 37.3; H 6.3; N 5.9
$C_8H_{16}O_4NSCl$. Calculated %: C 37.0; H 6.2; N 5.4

Methyl ester of N-(2-bromopropionyl)-3,3-dimethylcysteine. The methyl ester of 3,3-dimethylcysteine (3.2 g, i.e., 0.02 mole) was dissolved in absolute ether (150 ml), and a solution of 2,2 g (0.01 mole) of 2-bromopropionyl bromide in ether was added. The mixture was set aside at room temperature for twelve hours. The precipitated hydrobromide of the methyl ester of 3,3-dimethylcysteine was pressed off and washed with ether. The united ether solutions were washed with N HCl and with water, and were dried over magnesium sulfate. The ether was evaporated off until crystallization began. The crystals were filtered off and washed with a small amount of ether, and 1.4 g (50%) of the methyl ester of N-(2-bromopropionyl)-3,3-dimethylcysteine, m.p. 71-72°, was obtained.

Found %: C 36.3; H 5.41
$C_9H_{16}O_3NSBr$. Calculated %: C 36.2; H 5.3

S-(carboxymethyl)-3,3-dimethylcysteine (XIII). 3,3-Dimethylcysteine (0.75 g, i.e., 0.005 mole) was dissolved in 5 ml of water, and 5 ml of 2 N NaOH was added. Bromoacetic acid (0.7 g, i.e., 0.005 mole) was then added gradually. After two hours the mixture was acidified to Congo Red with N HCl and evaporated under reduced pressure. The dry residue was dissolved in absolute alcohol, and the solution was filtered; 1 ml of pyridine was added to remove HCl, and the mixture was set aside for five hours. The precipitate was filtered off and washed with absolute alcohol, and 0.3 g of S-(carboxymethyl)-3,3-dimethylcysteine, m.p. 147° with decomposition, was obtained.

Found %: C 39.4; H 6.05; N 6.4
$C_7H_{13}O_4NS$. Calculated %: C 40.5; H 6.2; N 6.7

2,2-Dimethyl-5-oxo-3-thiamorpholinecarboxylic acid (XIV). a) Pyridine (0.1 ml) was added to a solution of 0.1 g of the hydrochloride of S-(carboxymethyl)-3,3-dimethylcysteine in 4 ml of absolute alcohol. The mixture was set aside at room temperature for twelve hours. The alcohol was then evaporated off, 2 ml of water was added, and the precipitated 2,2-dimethyl-5-oxo-3-thiamorpholinecarboxylic acid was pressed off. After recrystallization from water the substance (XIV) melted at 172-173°. A mixture test with a sample prepared by a previously known method [3] showed no melting point depression.

b) S-(Carboxymethyl)-3,3-dimethylcysteine (0.2 g) was heated at 100° in a vacuum over phosphoric anhydride for three hours, and the substance (XIV), m.p. 172-173°, was obtained. Unlike the free acid, the hydrochloride of S-(carboxymethyl)-3,3-dimethylcysteine does not undergo cyclization under these conditions.

Methyl ester of N-(2,3-dibromopropionyl)-3,3-dimethylcysteine. A solution of 1.25 g (0.005 mole) of 2,3-dibromopropionyl chloride in 10 ml of absolute ether was added to a solution of 1.63 g (0.01 mole) of the methyl ester of 3,3-dimethylcysteine in 25 ml of absolute ether. The precipitated hydrochloride of the methyl ester of 3,3-dimethylcysteine was pressed off and washed with ether. The united ether solutions were washed with N HCl and with water, and were dried over magnesium sulfate. Ether was removed under reduced pressure until crystallization began, and a quantitative yield of the methyl ester of N-(2,3-dibromopropionyl)-3,3-dimethylcysteine, m.p. 92-93°, was obtained. After recrystallization from hot water it melted at 101-102°. The substance is readily soluble in ether, alcohol, and dioxane, but difficultly soluble in petroleum ether.

Found %: C 29.11; H 4.1; N 4.1

$C_9H_{15}O_3NSBr_2$. Calculated %: C 28.64; H 3.98; N 3.71

SUMMARY

1. It has been shown that 3,3-dimethylcysteine is readily acylated by means of acid anhydrides and acid chlorides and that it then forms only N-acyl derivatives.

2. 3,3-Dimethylcysteine is readily alkylated in aqueous alkaline solution, particularly by halogen-substituted acids, with formation of only S-alkyl derivatives. With acid chlorides of β-halo carboxylic acids, 3,3-dimethylcysteine forms derivatives of hexahydro-1,4-thiazepin-5-one.

3. It has been shown that the products of the S-alkylation of 3,3-dimethylcysteine with α-bromo carboxylic acids are readily converted into derivatives of 3-thiamorpholinone, which is an unusual case of the spontaneous acylation of an amino group by a carboxylic acid.

Received April 9, 1954

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

LITERATURE CITED

[1] A. Einhorn, Ann., 343, 207 (1905); 361, 113 (1908); H Conrad and H. Olcoff, J. Am. Chem. Soc., 70, 2673, 1948.

[2] K. Savard, et. al., J. Can. Res., 24, No. 1, 28 (1946).

[3] The Chemistry of Penicillin, 1949, 938.

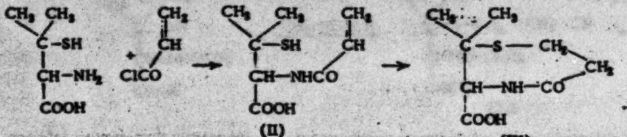
BLANK
PAGE

REACTIONS OF MERCAPTO AMINO ACIDS

COMMUNICATION 3. ACYLATION AND ALKYLATION OF 3, 3-DIMETHYLCYSTEINE

I. L. Knunyants, O. V. Kildisheva, and M. G. Linkova

We have previously shown that N-(3)chloropropiony)-3,3-dimethylcysteine readily undergoes cyclization in presence of alkali with formation of hexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid (I) [1]. When 3,3-dimethylcysteine is acylated with acryloyl chloride, N-acryloyl-3,3-dimethylcysteine (II) is readily formed, and in presence of alkali intramolecular reaction between the thiol group and the acryloyl residue occurs with formarion of the compound (III), identical with hexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid (I):

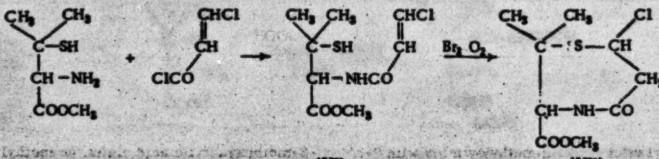


(II) (III)

When the methyl ester of 3,3-dimethylcysteine is acylated with acryloyl chloride, a quantitative yield is obtained of the methyl ester of N-acryloyl-3,3-dimethylcysteine (IV), which is again converted into a cyclic acid identical with (III) when hydrolyzed with alkali. With diazomethane, hexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid (III) is converted into the corresponding methyl ester (V).

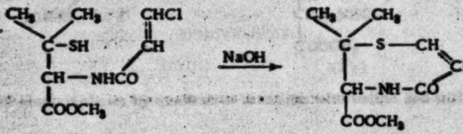
The possibility of the intramolecular addition of the thiol group of 3,3-dimethylcysteine to the double bond of the acrylic residue has thus been demonstrated.

Acylation of 3,3-dimethylcysteine methyl ester with 3-chloroacryloyl chloride yields the methyl ester of N-(3-chloroacryloyl)-3,3-dimethylcysteine (VI), which, unlike N-acryloyl-3,3-dimethylcysteine (II), cyclizes with difficulty, the product being the compound (VII):



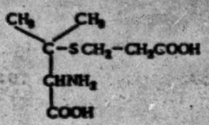
(VI) (VII)

Addition of the thiol group is not accelerated by ultraviolet radiation or by Triton B, and only in presence of benzoyl peroxide was the compound (VII) obtained in limited yield. In presence of alkali (VI) is readily converted into the unsaturated seven-membered ring compound (VIII):

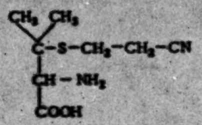


(VI) (VIII)

Addition of acrylic acid to 3,3-dimethylcysteine yields the already known S-(2-carboxyethyl)-3,3-dimethylcysteine (IX) [1]. Acrylonitrile reacts similarly with 3,3-dimethylcysteine, forming S-(2-cyanoethyl)-3,3-dimethylcysteine (X):



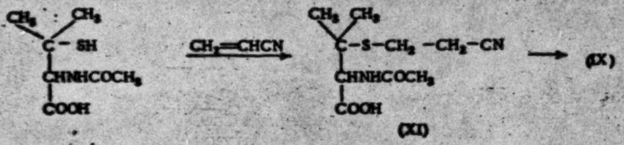
(IX)



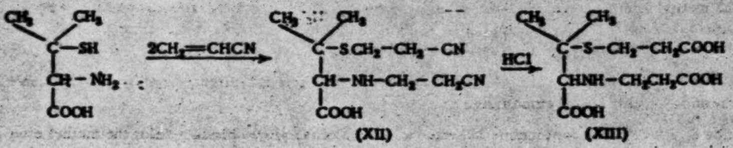
(X)

The structures of the compounds obtained, as S-derivatives of 3,3-dimethylcysteine, were proved by the following series of transformations.

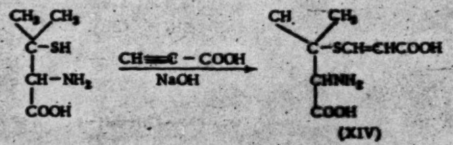
Compound (X) was readily converted by hydrolysis with hydrochloric acid into the dicarboxylic acid (IX), which was found to be identical with the dicarboxylic acid obtained both by the alkylation of 3,3-dimethylcysteine with 3-iodopropionic acid and also by the scission of hexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid [1]. The dicarboxylic acid was obtained also by the action of acrylonitrile on N-acetyl-3,3-dimethylcysteine, followed by hydrolysis of the addition product (XI) with hydrochloric acid:



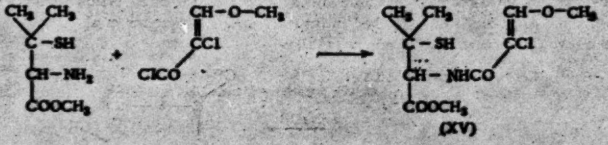
It should be noted that acrylonitrile adds to 3,3-dimethylcysteine much more readily than acrylic acid does. In presence of an excess of acrylonitrile, the amino group of 3,3-dimethylcysteine also reacts, and the N,S-disubstituted product (XII) is obtained; this dinitrile may be hydrolyzed to the tricarboxylic acid (XIII):



Dimethylcysteine readily adds to propiolic acid with formation of the dicarboxylic acid (XIV):

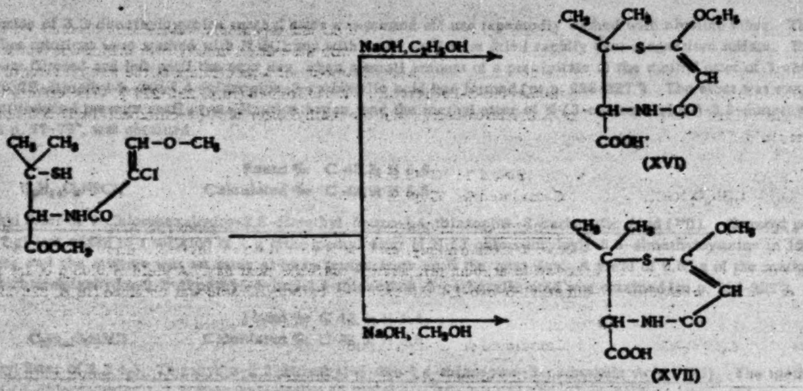


Acylation of the methyl ester of 3,3-dimethylcysteine with 2-chloro-3-methoxyacrylic acid yields the methyl ester of N-(2-chloro-3-methoxyacryloyl)-3,3-dimethylcysteine (XV):



The presence of a free thiol group is shown by qualitative reactions with iodine and with lead acetate (yellow precipitate of mercaptide).

Hydrolysis of the ester group of (XV) with an alcoholic solution of caustic soda yields the cyclic compound (XVI) with simultaneous elimination of HCl and replacement of the alkoxy group in the ring by the residue of the alcohol in which the alkali is dissolved. Thus, when the methyl ester of N-(2-chloro-3-methoxyacryloyl)-3,3-dimethylcysteine is treated with ethanolic caustic soda, the corresponding ethoxy derivative (XVI) is obtained, and when it is treated with methanolic alkali the product is the corresponding methoxy derivative (XVII):



With diazomethane, the ethoxy derivative is readily converted into the methyl ester of 7-ethoxy-2,3,4,5-tetrahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid.

EXPERIMENTAL

N-Acryloyl-3,3-dimethylcysteine (II). Sodium bicarbonate (1.2 g) was added to a solution of 0.45 g (0.003 mole) of 3,3-dimethylcysteine in 10 ml of water, which was then cooled to 0°. The mixture was then shaken while 0.9 g (0.009 mole) of acryloyl chloride was added in portions. After two hours the temperature was raised to that of the room, and the mixture was filtered and carefully acidified to Congo Red with N HCl. The precipitated N-acryloyl-3,3-dimethylcysteine was pressed off and recrystallized from water; m.p. 143-144°.

	Found %: C 47.38; H 6.6; S 15.8
$C_8H_{13}O_3NS$.	Calculated %: C 47.29; H 6.4; S 15.75

The resulting N-acryloyl-3,3-dimethylcysteine was dissolved in 0.5 N NaOH, and the solution was set aside at room temperature for twelve hours. Acidification yielded the known hexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid [1]; m.p. 270° with decomposition.

Methyl Ester of N-Acryloyl-3,3-dimethylcysteine (IV). A solution of 0.9 g (0.01 mole) of acryloyl chloride in 50 ml of absolute ether was added to a solution of 3.2 g (0.02 mole) of the methyl ester of 3,3-dimethylcysteine in 150 ml of absolute ether. The mixture was set aside at room temperature for twelve hours. The precipitated hydrochloride of the methyl ester of 3,3-dimethylcysteine was pressed off and washed with absolute ether. The united ether solutions were washed with N HCl and with water, and were dried over magnesium sulfate. After removal of ether, the methyl ester of N-acryloyl-3,3-dimethylcysteine was filtered off and washed with a small amount of absolute ether. The yield was 1.7 g; m.p. 70-72°.

	Found %: C 49.9; H 7.0; S 14.5 N 6.44
$C_9H_{15}O_3NS$.	Calculated %: C 49.8; H 6.9; S 14.7; N 6.45

Methyl Ester of Hexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic Acid (V). An alcoholic solution of caustic soda (5 ml of 0.5 N) was added to 0.2 g of the methyl ester of N-acryloyl-3,3-dimethylcysteine, and the mixture was set aside for two hours. Alcohol was removed under reduced pressure, and the residue was dissolved in 5 ml of water and acidified with N HCl. The precipitate of hexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid was pressed off; m.p. 176-177° with decomposition; yield 0.12 g. A mixture test with the compound (I) [1] showed no depression. The hexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid was dissolved in alcohol, and an ether solution of diazomethane was added. After partial removal of solvent a precipitate formed of the methyl ester of hexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid, m.p. 230-240° with decomposition.

	Found %: C 50.16; H 7.2
$C_9H_{15}O_3NS$.	Calculated %: C 49.8; H 6.9

Methyl Ester of N-(3-chloroacryloyl)-3,3-dimethylcysteine (VI). A solution of 1.25 g (0.01 mole) of 3-chloroacryloyl chloride in 50 ml of absolute ether was added to a solution of 3.2 g (0.02 mole) of 3,3-dimethylcysteine methyl ester in 150 ml of absolute ether. The mixture was left for 2-3 hours at room temperature. The precipitated hydrochloride of 3,3-dimethylcysteine methyl ester was pressed off and repeatedly washed with absolute ether. The united ether solutions were washed with N HCl and with water, and were dried rapidly over magnesium sulfate. The solution was filtered and left until the next day, when a small amount of a precipitate of the methyl ester of 7-chlorohexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid had formed (m.p. 226-227°). The ether was evaporated under reduced pressure until crystallization began, and the methyl ester of N-(3-chloroacryloyl)-3,3-dimethylcysteine, m.p. 77-78°, was obtained.

Found %: C 43.3; H 5.6
$C_9H_{14}O_3NSCl$. Calculated %: C 42.9; H 5.5

Methyl Ester of 7-Chlorohexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic Acid (VII). Benzoyl peroxide (0.2 g) was added to a solution of 1 g of the methyl ester of N-(3-chloroacryloyl)-3,3-dimethylcysteine in 100 ml of ether, and the mixture was set aside at room temperature until the next day. A yield of 0.05 g of the methyl ester of 7-chlorohexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid was obtained (m.p. 226-227°).

Found %: C 43.4; H 5.4
$C_9H_{14}O_3NSCl$. Calculated %: C 42.9; H 5.5

Methyl Ester of 2,3,4,5,-Tetrahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic Acid (VIII). The methyl ester of N-(3-chloroacryloyl)-3,3-dimethylcysteine (0.125 g) was dissolved in 100 ml of absolute ether, and an equivalent amount of methanolic N NaOH was added gradually. The mixture was stirred for two hours. Ether was removed under reduced pressure, and the residue was pressed off and washed with water. The product was 0.17 g of the methyl ester of 2,3,4,5-tetrahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid, m.p. 155-160°.

Found %: C 48.7; H 6.4; N 6.48
$C_9H_{13}O_3NS$. Calculated %: C 50.2; H 6.05; N 6 51

The aqueous mother liquor contained the theoretical amount of sodium chloride (determined by Volhard's method).

S-(2-Carboxyethyl)-3,3-dimethylcysteine (IX). a) A solution of 0.3 g (0.002 mole) of 3,3-dimethylcysteine in 4 ml of water was mixed with 0.15 g (0.002 mole) of acrylic acid, and 10% ammonia was added to pH 7. The mixture was heated in a water bath at 100° for 90 minutes, cooled, acidified to Congo Red, and evaporated under reduced pressure. The dry residue was dissolved in absolute alcohol, and 0.3 ml of pyridine was added to remove HCl. The precipitated S-(2-carboxyethyl)-3,3-dimethylcysteine was filtered off and washed with alcohol. A yield of 0.07 g was obtained of a substance of m.p. 177-179°. A mixture test with the S-(2-carboxyethyl)-3,3-dimethylcysteine obtained from 3,3-dimethylcysteine and 3-iodopropionic acid showed no depression.

b) Acrylonitrile (0.2 g) was added to a solution of 0.57 g (0.003 mole) of N-acetyl-3,3-dimethylcysteine in 3.5 ml of caustic soda solution (0.16 g of NaOH). The temperature rose spontaneously to 39°. After 30 minutes, 4.5 ml of hydrochloric acid (sp.gr 1.19) was added, and the mixture was heated for two hours under reflux. The solution was then evaporated under reduced pressure, and the dry residue was dissolved in absolute alcohol. The solution was filtered, and S-(2-carboxyethyl)-3,3-dimethylcysteine, m.p. 178-179°, was isolated as described above.

S-(2-Cyanoethyl)-3,3-dimethylcysteine (X). 3,3-Dimethylcysteine (0.45 g, i.e. 0.003 mole) was dissolved in 5 ml of water containing 0.12 g of caustic soda. The resulting alkaline solution was stirred, and 0.2 g of acrylonitrile was gradually added at 25-26° over a period of one hour. The solution was acidified with 80% acetic acid and diluted with twice its volume of ethanol. The precipitated S-(2-cyanoethyl)-3,3-dimethylcysteine was filtered off and recrystallized from 50% alcohol. The product was 0.5 g of the substance (X), m.p. 181-182°.

Found %: S 15.3; N 13.65
$C_8H_{14}O_2N_2S$. Calculated %: S 15.8; N 13.86

N,S-Bis(2-cyanoethyl)-3,3-dimethylcysteine (XII). 3,3-Dimethylcysteine (0.6 g, i.e. 0.004 mole) was dissolved in caustic soda solution (containing 0.16 g of NaOH), and 0.3 g (0.008 mole) of acrylonitrile was added. The temperature rose spontaneously to 32°. After 30 minutes the solution was acidified with 80% acetic acid and diluted with five times its volume of ethanol. The precipitated N,S-bis(2-cyanoethyl)-3,3-dimethylcysteine was filtered off and washed with alcohol. The product was 0.5 g of the substance (XII), m.p. 149-150°.

Found %: C 51.9; H 6.9; S 12.5; N 16.4
$C_{11}H_{17}O_2N_3S$. Calculated %: C 51.8; H 6,66; S 12.5; N 16.4

N,S-Bis(2-carboxyethyl)-3,3-dimethylcysteine (XIII). A mixture of 0.5 g of N,S-bis(2-cyanoethyl)-3,3-dimethylcysteine and 10 ml of 15% HCl was heated under reflux for five hours and then evaporated under reduced pressure. The dry residue was dissolved in absolute alcohol, and the solution was filtered. Addition of 0.5 ml of pyridine precipitated N,S-bis(2-carboxyethyl)-3,3-dimethylcysteine m.p. 187-188°, in quantitative yield.

Found %: C 45.07; H 6.58; S10.56; N 4.89

$C_{11}H_{19}O_6NS$. Calculated %: C 45.05; H 6.51 S10.92; N 4.77

S-(2-Carboxyvinyl)-3,3-dimethylcysteine (XIV). Propiolic acid (0.2 g, i.e. 0.003 mole) was added to a solution of 0.45 g (0.003 mole) of 3,3-dimethylcysteine in 7 ml of N NaOH. The mixture was set aside for 3-4 hours at room temperature, acidified to Congo Red with N HCl, and evaporated to dryness. The residue was dissolved in absolute alcohol, and the solution filtered. Pyridine (0.5 ml) was then added, and the solution was set aside at room temperature for twelve hours. The product was 0.2 g of S-(2-carboxyvinyl)-3,3-dimethylcysteine, m.p. 153-154°.

Found %: S 14.6; N 6.47

$C_8H_{13}O_4NS$. Calculated %: S 14.6; N 6.35

Methyl Ester of N-(2-Chloro-3-methoxyacryloyl)-3,3-dimethylcysteine (XV). A solution of 8 g of 2-chloro-3-methoxyacrylic acid in 100 ml of absolute ether was added to a solution of 17 g of the methyl ester of 3,3-dimethylcysteine in 250 ml of absolute ether, and the mixture was set aside at room temperature for twelve hours. On the next day the hydrochloride of the methyl ester of 3,3-dimethylcysteine was pressed off and carefully washed with absolute ether. The united ether solutions were washed with N HCl and with water, and were dried over magnesium sulfate. Ether was removed under reduced pressure until crystallization began. The yield of the methyl ester of N-(2-chloro-3-methoxyacryloyl)-3,3-dimethylcysteine was 12.6 g (86%). After recrystallization from ether it melted at 64-66°. The substance is readily soluble in alcohol and ether, but insoluble in water.

Found %: C 42.67; H 5.86; S 11.23; Cl 12.5; N 5.1

$C_{10}H_{16}O_4NSCl$. Calculated %: C 42.7; H 5.7; S 11.3; Cl 12.6; N 4.97

7-Ethoxy-2,3,4,5,-tetrahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic Acid (XVI). The methyl ester of N-(2-chloro-3-methoxyacryloyl)-3,3-dimethylcysteine (2.8 g, i.e. 0.01 mole) was dissolved in 12 ml of 2 N ethanolic NaOH, and the solution was set aside at room temperature for twelve hours. Absolute ether (20 ml) was then added, and the precipitate that formed was filtered off, dissolved in the least possible amount of water, and acidified with 2 N HCl until precipitation was complete. The precipitate of 7-ethoxy-2,3,4,5-tetrahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid was filtered off and washed with water. After recrystallization from alcohol the substance (XVI) melted at 187-188°. The yield was 0.9 g (40.5 %).

Found %: C 48.5; H 6.17; S 12.78; N 5.88; OC_2H_5 18.07

$C_{10}H_{15}O_4NS$. Calculated %: C 48.8; H 6.12; S 13.06; N 5.68 OC_2H_5 18.3

2,3,4,5 -Tetrahydro-7-methoxy-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic Acid (XVII). The methyl ester of N-(2-chloro-3-methoxyacryloyl)-3,3-dimethylcysteine (1.4 g, i.e. 0.005 mole) was dissolved in 7 ml of 2 N methanolic NaOH, and the solution was set aside at room temperature for twelve hours. Absolute ether (10 ml) was added, and the resulting precipitate was filtered off, dissolved in the least possible amount of water, and acidified with 2 N HCl until precipitation was complete. The precipitate of 2,3,4,5-tetrahydro-7-methoxy-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid was pressed off and washed with water. After recrystallization from 50% alcohol the substance (XVII) melted at 216-219°. The yield was 0.7 g (60.5%).

Found %: C 46.52; H 5.66; N 6.05

$C_9H_{14}O_4NS$. Calculated %: C 46.55; H 5.63; N 6.0

Methyl Ester of 7-Ethoxy-2,3,4,5-tetrahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic Acid (XVIII). A solution of 0.5 g of the substance (XVI) in 1 ml of methanol was treated with an ether solution of diazomethane until nitrogen ceased to be evolved. Alcohol and ether were removed under reduced pressure until crystallization began. The precipitate was filtered off and recrystallized from ether. The product was 0.3 g (58%) of the substance (XVIII), m.p. 86-88°. The substance is very readily soluble in alcohol and ether.

Found %: C 50.82; H 6.67; N 5.46

$C_{11}H_{17}O_4NS$ Calculated %: C 50.96; H 6.56; N 5.4

SUMMARY

1. A number of substituted N-acryloyl derivatives of 3,3-dimethylcysteine, having bromine, chlorine, and methoxyl in the acyl residue, have been prepared.

2. It has been shown that these derivatives undergo cyclization by the intramolecular addition of the thiol group of the dimethylcysteine to the double bond of the acryloyl residue with formation of hexahydro-1,4-thiazepin-5-ones.

3. It has been shown that, in the reaction of 3,3-dimethylcysteine with unsaturated acids and their derivatives, the main process occurring is the addition of the thiol group of the dimethylcysteine to the double bond with formation of S-carboxyalkyl derivatives of 3,3-dimethylcysteine.

Received April 9, 1954

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

LITERATURE CITED

[1] I. L. Knunyants and M. G. Linkova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955 No.1, 62.*

---

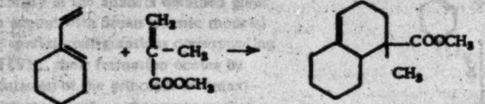
* Consultants Bureau Translation, this issue, p. 53.

STEREOCHEMISTRY OF CYCLIC COMPOUNDS

COMMUNICATION 4. CONDENSATION OF 1-VINYLCYCLOHEXENE WITH CITRACONIC ANHYDRIDE

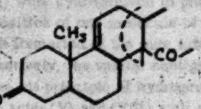
I. N. Nazarov, V. F. Kucherov, and V. M. Andreev

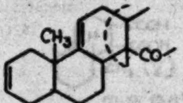
A study of the condensation of 1-vinylcyclohexene with such dienophiles as acrolein, methacrylic acid, and methyl methacrylate [1] has shown that in this reaction predominant formation of the ortho isomer occurs:



The dimerization of 1-vinylcyclohexene [2] and its condensation with 2-cyclohexen-1-one [3] also proceed according to this ortho-condensation scheme. The condensation of 1-vinylcyclohexene with 2,4-dimethyl-2-cyclopenten-1-one [4] is more complex, but in this case also, the reaction products have the structure of ortho adducts.

Studies by Nazarov and coworkers [5] have shown that, when various bicyclic vinylcycloalkenes condense with α,β-unsaturated cyclic ketones, the product is a mixture of stereoisomeric tetracyclic ketones of ortho structure (the so-called "inverted" steroid structure).





In those diene condensations in which the bicyclic diene has one aromatic ring, a mixture of the two possible ortho and meta adducts is formed, as was shown in the case of the condensation of 1,2-dihydro-7-methoxy-4-vinylnaphthalene with citraconic anhydride [6] and with 2-cyclopenten-1-one [7].

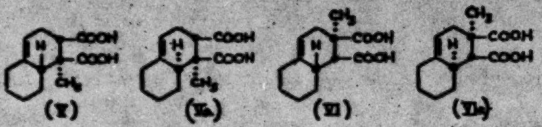
In such condensations, the course of the reaction presents great interest not only in relation to structural questions, but also with respect to questions of stereochemistry, which, as is well known, are of very great importance in the synthesis of polycyclic compounds related to the steroids. With a view to the further systematic study of the structural and spatial aspects of the course of the diene synthesis, we have made a detailed investigation of the condensation of 1-vinylcyclohexene (I) with citraconic anhydride (II). We have found that prolonged heating (11-15 hours) of the mixture of reactants (40% excess of diene) at 100° gave a 92% yield of a mixture of crystalline and liquid anhydrides (III) and (IV). Hydrolysis of this mixture with 3% aqueous caustic soda resulted in the isolation of two isomeric crystalline cis acids (V) and (VI) in the ratio of 5 : 1 approximately. The structures of these acids were proved by dehydrogenation in presence of palladized charcoal (10% Pd) at 360-370° for 18 hours. The cis acid (V) then yielded 1-methylnaphthalene, identified as the picrate, m.p. 138.5 - 140°, undepressed by admixture with an authentic sample. The acid (VI), when dehydrogenated under the same conditions, yielded 2-methylnaphthalene, characterized as the picrate, m.p. 114-114.5°, also undepressed by admixture with an authentic sample.

These results show that the cis acids (V) and (VI) are structural isomers, and that in the present case the two possible structures, ortho and meta, are formed, with considerable predominance of the ortho isomer (V).

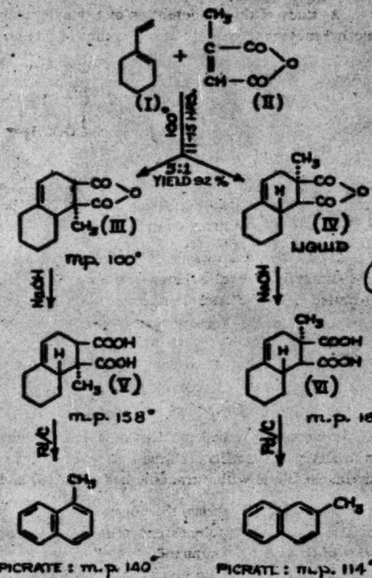
No other products were isolated in the condensation of 1-vinylcyclohexene with citraconic anhydride at 100°. At a lower temperature (20°) the reaction is slower, and under these conditions only the cis anhydride (III) was isolated. After condensation at a high temperature (220-230°) and subsequent hydrolysis, the acids (V) and (VI) were again isolated in about the same proportions (5:1). The cis anhydride (III) is thermally stable, being practically unchanged by heating at 200° for two hours.

The cis structure of the acids (V) and (VI) follows from the method of preparation, and the readiness with which the double bond undergoes hydrogenation and its displacement in presence of a mixture of hydrochloric and acetic acids (see below) indicate that it occurs in the normal position (the 4-position).

In accordance with the method of synthesis (the cis principle of the diene condensation), each of the cis acids (V) and (VI), with their three asymmetric carbon atoms (bold points in the formulas), can exist in the form of two stereoisomers:



(1



(2

The fact that only one isomer is formed for each structural species indicates that, under our conditions, quite definite steric orientation occurs in the diene synthesis. The thermal stability of the adducts obtained gives us reason to suppose (in accord with Stuart atomic models) that these adducts have spatial configurations corresponding to the formulas (V) and (VI); their formation occurs by "exo-addition" with violation of the principle of "maximum accumulation of unsaturation", a phenomenon that has been observed several times before in diene condensations at high temperatures [8].

A number of the reactions of the cis acids (V) and (VI) were studied, and these enabled us to examine their structures in greater detail. When cis-1,2,3,5,6,8,8a-octahydro-1-methyl-1,2-naphthalenedicarboxylic acid (V) and its anhydride (III) were hydrogenated in presence of a platinum catalyst, addition of one molecule of hydrogen readily occurred with formation of the pure substances (VIII) and (VII) respectively, the spatial configurations of which follow from the cis principle of hydrogenation. Treatment of the cis acids (V) and (VIII) with acetyl chloride yielded the cis anhydrides (III) and (VII), and treatment with diazomethane yielded the corresponding cis diesters (IX) and (X); the latter was readily obtained also by hydrogenation of the unsaturated cis diester (IX) in presence of a platinum catalyst.

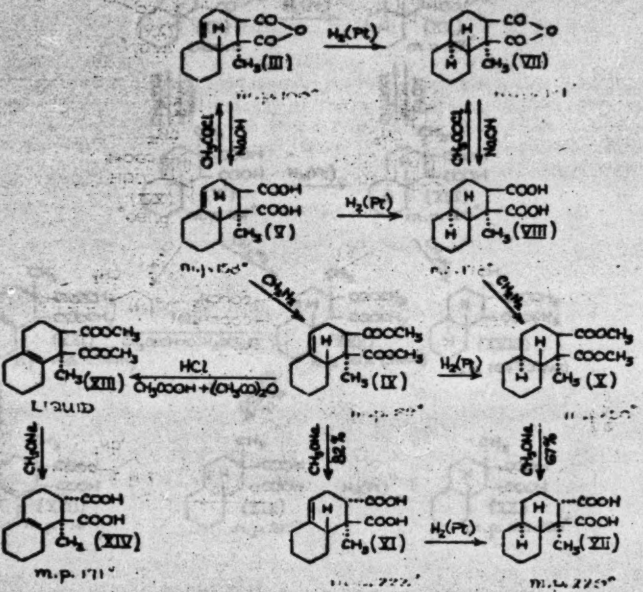
Thus, the hydrogenation of the cis anhydride (III), acid (V), and ester (IX) is sterically selective, which is to be explained by the screening effect of the cis substituents at C-1, C-2, and C-8a (see below), as a result of which the hydrogen adds at the double bond at the side opposite to these substituents (the less screened side).

By isomerization of the cis diesters (IX) and (X) in presence of sodium methoxide, good yields were readily obtained of the corresponding trans-1,2,3,5,6,7,8,8a-octahydro-1-methyl-1,2-naphthalenedicarboxylic acid (XI), m.p. 222°, and trans-decahydro-1-methyl-1,2-naphthalenedicarboxylic acid (XII), m.p. 229°.

The crystalline cis diester (IX), when treated at 60° with a mixture of acetic anhydride and acetic acid saturated with dry hydrogen chloride, isomerized into the liquid diester (XIII) with displacement of the double bond, and this, when isomerized in presence of sodium methoxide, yielded the new trans acid (XIV), m.p. 170-171°. Unlike the compounds (IX) and (XI), the cis diester (XIII) and the trans acid (XIV) showed little tendency to undergo hydrogenation in presence of a platinum catalyst under the usual conditions, a fact that confirms the inter-ring position of the double bond.

The above-described reactions were carried out also for the case of the isomeric cis-1,2,3,5,6,7,8,8a-octahydro-2-methyl-1,2-naphthalenedicarboxylic acid (VI). The unsaturated cis anhydride (IV) and the corresponding acid (VI) were readily hydrogenated in presence of a platinum catalyst with formation of the pure individual anhydride

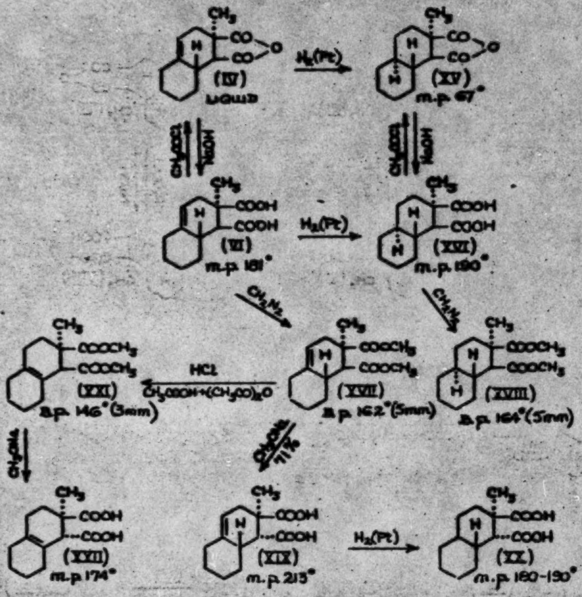
(XV) and acid (XVI). In this case again, therefore, the hydrogenation of the cis anhydride (IV) and the cis acid (VI) proceed in a selective manner, which is to be explained by the same steric factors as in the case of the hydrogenation of the cis compounds (III), (V), and (IX).



Treatment of the cis acids (VI) and (XVI) with diazomethane yielded the corresponding cis diesters (XVII) and (XVIII). Isomerization of the cis diester (XVII) in presence of sodium methoxide gave a good yield of trans-1,2,3,5,6,7,8,8a-octahydro-2-methyl-1,2-naphthalenedicarboxylic acid (XIX), m.p. 213°. The hydrogenation of this trans acid in presence of a platinum catalyst is now no longer selective, and a mixture of isomeric saturated acids (XX), m.p. 180-190°, was obtained attempts to separate these by crystallization were not successful. It must be pointed out that the catalytic hydrogenation at platinum of the trans acid (XI), unlike that of the trans acid (XIX), proceeds in a sterically selective manner. This interesting fact indicates that in such compounds the screening of the double bond is effected by cis substituents at (C-1) — (C-8a), and not by substituents at (C-1) — (C-2). When there is a trans disposition of substituents at (C-1) — (C-8a), as in the trans acid (XIX) (see Communication 5), sterically oriented hydrogenation becomes impossible. This conclusion is confirmed also by an examination of Stuart atomic models.

When treated with a mixture of acetic anhydride and acetic acid saturated with hydrogen chloride, the cis diester (XVII) yields the new liquid diester (XXI), which isomerizes in presence of sodium methoxide into the trans acid (XXII), m.p. 174°. The cis diester (XXI) and the trans acid (XXII), in which the double bond is in the inter-ring position, are not hydrogenated at a platinum catalyst under normal conditions.

All of these transformations of the isomeric acids (V) and (VI) show that they are cis-1,2,3,5,6,7,8,8a-octahydro-1- and -2-methyl-1,2-naphthalenedicarboxylic acids having the spatial configuration corresponding to the more stable structure formed by "exo-addition".



EXPERIMENTAL

Condensation of 1-Vinylcyclohexene with Citraconic Anhydride

A mixture of 50 g of 1-vinylcyclohexene (I) [9], 36 g of citraconic anhydride [10], and a little (about 0.2 g) of pyrogallol was heated in a boiling water bath for eleven hours and then set aside at room temperature for one day The precipitated crystalline product was carefully pressed off on the filter and washed with petroleum ether, and 30.7 g of a substance of m.p. 92-96° was obtained. The liquid residue obtained after removal of petroleum ether was heated in a boiling water bath for a further four hours, and was then set aside at 0° for two days. A further 3.6 g of a crystalline product, m.p. 77-89°, separated. The liquid residue remaining after removal of excess of 1-vinylcyclohexene and a small amount of citraconic anhydride by distillation was then vacuum-distilled, and yielded 22 g of a light-yellow viscous oil, b.p. 157-159° (4 mm), n_D^{20} 1.5130. From this oil, after being dissolved in an equal volume of petroleum ether and then allowed to stand at 0° overnight, a further 5.3 g of crystals, m.p. 75-84°, separated. The total yield of crystalline reaction product was 39.6 g. After recrystallization from a mixture of absolute ether and petroleum ether, 34.7 g of the pure cis anhydride (III) was obtained in long coarse needles, m.p. 99-100°

Found %: C 71.02; 71.18; H 7.36; 7.39
$C_{13}H_{16}O_3$ Calculated %: C 70.92; H 7.28

The liquid reaction product was repeatedly distilled and yielded 15.7 g of the liquid cis anhydride (IV), b.p. 140-142.5° (2 mm), n_D^{18} 1.5138.

Found %: C 71.39; 71.29; H 7.60; 7.50
$C_{13}H_{16}O_3$ Calculated %: C 70.92; H 7.28

The analysis of the cis anhydride (IV) showed somewhat high carbon and hydrogen contents, which may be explained by contamination with a little of the dimer of 1-vinylcyclohexene, which we did not succeed in removing by distillation.

The overall yield of condensation products was about 92% on the amount of citraconic anhydride that reacted.

cis-1,2,3,5,6,7,8,8a-Octahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (V)

A mixture of 18 g of the crystalline cis anhydride (III), m.p. 99-100°, and 250 ml of 3% aqueous caustic soda was stirred at 60° until solution was complete (90 minutes). The resulting solution was acidified to Congo Red with 1 : 1 hydrochloric acid, cooling being applied. The oil that at first separated rapidly crystallized as the mixture was stirred, and 18.5 g of a crystalline substance, m.p. 152-157°, was obtained. Recrystallization from a mixture of benzene and petroleum ether yielded 17.1 g of the cis acid (V), m.p. 157-158° with decomposition.

Found %: C 65.30; 65.60; H 7.62; 7.58
$C_{13}H_{18}O_4$ Calculated %: C 65.52; H 7.53

When the cis acid (V) was boiled with acetyl chloride, the original cis anhydride (III), m.p. 98-99°, was obtained.

cis-1,2,3,5,6,7,8,8a-Octahydro-2-methyl-1,2-naphthalenedicarboxylic Acid (VI)

A mixture of 15.7 g of the liquid cis anhydride (IV) and 200 ml of 3% aqueous caustic soda was stirred at 60° until solution was complete (90 minutes). The dark-brown solution was treated with active charcoal and filtered, and was then acidified to Congo Red with hydrochloric acid. On standing, the thick oil that separated partially solidified. The crystalline product was carefully pressed off on the filter, and the oily contamination was washed out with a 1 : 1 mixture of acetone and petroleum ether. The product was 6.8 g of a crystalline substance, m.p. 168-172°. Two recrystallizations from a 2 : 1 mixture of benzene and acetone yielded 5 g of the cis acid (VI), having a constant melting point of 181-181.5° with decomposition.

Found %: C 65.55; 65.62; H 7.74; 7.70
$C_{13}H_{18}O_4$ Calculated %: C 65.52 H 7.53

Conversion of the Cis Acid (VI) into the Anhydride (IV)

A mixture of 0.55 g of the cis acid (VI) (m.p. 180-181°) and 5.5 ml of acetyl chloride was boiled for one hour. Acetyl chloride was distilled off, and the residue was vacuum-distilled, yielding 0.4 g of the cis anhydride (IV), b.p. 157.5-158.5° (4 mm), n_D^{22} 1.5126.

Dehydrogenation of the Cis Acid (V)

A mixture of 5 g of the cis acid (V), m.p. 157-158°, 30 ml of cryoscopic benzene, and 1 g of palladized charcoal (10% Pd) was heated in an autoclave in an atmosphere of nitrogen for 18 hours at 360-370°. The mixture was filtered, the benzene was driven off, and the residue was vacuum-distilled. The product (1.3 g, b.p. 115-117°/ 19 mm) was again distilled under atmospheric pressure, and 0.6 g of a hydrocarbon, b.p. 237-238°, n_D^{21} 1.6080, was obtained.

In order to prepare the picrate, a solution of 0.5 g of the hydrocarbon in 2 ml of absolute ethanol was added to a warm solution of 0.81 g of picric acid in 8 ml of absolute ethanol. The voluminous precipitate of picrate was filtered off and recrystallized from ethanol; it then melted at 138.5-140°, undepressed by admixture with an authentic sample of 1-methylnaphthalene picrate (m.p. 139.5-141°). For 1-methylnaphthalene the literature [11] gives b.p. 241°, and m.p. of picrate 141-142°.

Dehydrogenation of the Cis Acid (VI)

From 1.2 g of the cis acid (VI), m.p. 181.5°, the above procedure yielded 0.6 g of a hydrocarbon, b.p. 234-240° and n_D^{22} 1.6010. The picrate melted at 114-115° and showed no depression when mixed with an authentic sample of 2-methylnaphthalene picrate (m.p. 115-116°).

cis-Decahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (VIII)

The cis acid (V) (2g; m.p. 157-158°) was dissolved in glacial acetic acid (25 ml) and hydrogenated over platinum oxide, when 236 ml (21°, 750 mm) of hydrogen was absorbed (one double bond required 230 ml). Acetic acid was distilled off under reduced pressure, and the crystalline residue was dissolved with the aid of heat in 20 ml of 30% aqueous caustic soda. The solution was filtered and acidified with dilute hydrochloric acid. The precipitated oil rapidly crystallized, and recrystallization from acetone yielded 1.5 g of the saturated cis acid (VIII), m.p. 177.5-178.5° with decomposition.

Found %: C 64.79; 65.00; H 8.30; 8.23

$C_{13}H_{20}O_4$. Calculated %: C 65.01; H 8.33

Anhydride of cis-Decahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (VII)

The unsaturated cis anhydride (III) (700 mg) was dissolved in acetic acid (10 ml) and hydrogenated over platinum oxide, when one molecular proportion (83 ml) of hydrogen was absorbed. The catalyst was filtered off, and the solvent was driven off under reduced pressure; the crystalline residue was washed on the filter with petroleum ether. The product was 620 mg of the saturated cis anhydride (VII), m.p. 127-129°, which, after crystallization from petroleum ether, melted at 130-131°.

Found %: C 70.34; 70.12; H 8.07; 7.92

$C_{13}H_{18}O_3$. Calculated %: C 70.21 H 8.15

Hydrolysis of the saturated cis anhydride (VII) with 3% caustic soda gave a quantitative yield of the saturated cis acid (VIII), m.p. 177-178°; and this, when boiled with acetyl chloride, gave the cis anhydride (VII), m.p. 130-131°, in good yield.

Dimethyl Ester of cis-1,2,3,5,6,7,8,8a-Octahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (IX)

An excess of an ether solution of diazomethane was added slowly to a cooled suspension of 6 g of the cis acid (V) (m.p. 157-158°) in 100 ml of ether. The ether was distilled off, and the crystalline residue was washed on the filter with a mixture of diethyl ether and petroleum ether (1 : 7). The product was 6.2 g of the cis diester (IX), m.p. 65-67°, and this, after crystallization from a small amount of ether, had a constant melting point of 68-69°.

Found %: C 67.95; 67.85; H 8.51; 8.38

$C_{15}H_{22}O_4$. Calculated %: C 67.69; H 8.33

Dimethyl Ester of cis-Decahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (X)

The saturated cis acid (VIII) (2.8 g) was treated as described above with an ether solution of diazomethane. The ether was driven off, and the liquid reaction product was vacuum-distilled, when 2.6 g of a viscous liquid, b.p. 165-167° (5 mm) and n$^{20}_{D}$ 1.4908, was obtained. On standing, this slowly crystallized, and recrystallization from a small amount of petroleum ether yielded the crystalline cis diester (X), m.p. 49-50.5°.

Found %: C 67.03; 67.24; H 8.94; 9.16

$C_{15}H_{24}O_4$. Calculated %: C 67.16; H 9.01

The same saturated cis diester (X) may be prepared by hydrogenation of the cis diester (IX) over platinum oxide in acetic acid.

trans-1,2,3,5,6,7,8,8a-Octahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (XI)

The cis diester (IX) (2.5 g) was added to a solution of 4.3 g of sodium in 160 ml of absolute methanol, and the mixture was boiled under reflux for 15 hours. Methanol, distilled off until the bulk had been reduced to one-quarter, 50 ml of water was added, and the solution was boiled for a further three hours. The solution was evaporated to dryness under reduced pressure, and the residue was dissolved in the least possible amount of water and acidified with hydrochloric acid. An oil separated and gradually solidified, yielding 2.0 g of a crystalline substance, m.p. 195-207°. Recrystallization from 70% aqueous methanol yielded 1.8 g of the pure trans acid (XI), m.p. 221-222° with decomposition. The yield was 82%.

Found %: C 65.40; 65.53; H 7.63; 7.50

$C_{13}H_{18}O_4$. Calculated %: C 65.52; H 7.53

trans-Decahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (XII)

1. The cis diester (X) (2.6 g) was added to a solution of sodium methoxide prepared from 4.5 g of sodium and 150 ml of methanol, and the mixture was boiled for 15 hours. After the above-described treatment, 1.9 g of a crystalline substance, m.p. 210-225°, was isolated, and this, when crystallized from 50% aqueous acetone, yielded 1.6 g (67%) of the pure trans acid (XII) in the form of fine needles, m.p. 228-229° with decomposition.

Found %: C 64.81; 64.85; H 8.49; 8.40

$C_{13}H_{20}O_4$. Calculated %: C 65.01 H 8.33

2. The unsaturated trans acid (XI) (470 mg) was dissolved in methanol (10 ml) and hydrogenated in presence of platinum oxide and chloroplatinic acid, one molecular proportion of hydrogen (55 ml, 26°, 743 mm) being absorbed. The catalyst was filtered off, and the solvent removed under reduced pressure. The product was 400 mg of an acid of m.p. 199-204°. Two crystallizations from 50% aqueous acetone yielded the trans acid (XII) of m.p. 228-229°, undepressed by admixture of the above-described sample.

Dimethyl Ester of cis-1,2,3,4,5,6,7,8-Octahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (XIII)

The dimethyl ester of cis-1,2,3,5,6,7,8,8a-octahydro-1-methyl-1,2-naphthalenedicarboxylic acid (IX) (2.4 g; m.p. 69°) was added to 20 ml of a mixture of two parts of acetic anhydride and one part of glacial acetic acid saturated at 20° with dry hydrogen chloride, and the solution was heated at 60° for one hour. The solvents were removed under reduced pressure, and distillation of the liquid reaction product yielded 1.6 g of the cis diester (XIII), b.p. 153-154° (5 mm), n_D^{19} 1.4985.

Found %: C 67.79; 67.60; H 8.33; 8.45

$C_{15}H_{22}O_4$. Calculated %: C 67.69; H 8.33

trans-1,2,3,4,5,6,7,8-Octahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (XIV)

The cis diester (XIII) (2.0 g) was added to a solution of 5 g of sodium in 150 ml of absolute methanol, and the mixture was boiled for 15 hours. The methanol was driven off under reduced pressure, and the residue was dissolved in water (40 ml) and boiled for a further five hours. The solution was treated with charcoal and filtered; it was then evaporated to a thick slurry in a porcelain dish on a water bath. The crystalline product was filtered off and dissolved in 10 ml of water. The solution was acidified with hydrochloric acid, and the precipitated oil rapidly solidified as the mixture was stirred. The product was 1.4 g of a substance melting at 145-152°. Two recrystallizations from 40% aqueous methanol yielded the trans acid (XIV), which had a constant melting point of 170-171°.

Found %: C 65.55; 65.55; H 7.65; 7.50

$C_{13}H_{18}O_4$. Calculated %: C 65.52; H 7.53

Found: M 236.4 (by titration with NaOH)

Calculated: M 238.3

The trans acid (XIV) gave a positive reaction with tetranitromethane and was not hydrogenated in presence of platinum oxide under the usual conditions.

cis-Decahydro-2-methyl-1,2-naphthalenedicarboxylic Acid (XVI)

The cis acid (VI) (200 mg) was dissolved in glacial acetic acid (5 ml) and hydrogenated in presence of platinum oxide, one molecular proportion of hydrogen (22 ml, 21°, 750 mm) being absorbed. The catalyst was filtered off, and the acetic acid was distilled off under reduced pressure. The thick liquid residue crystallized when treated with benzene. Crystallization from a mixture of benzene and petroleum ether yielded 120 mg of the pure cis acid (XVI), m.p. 189-190° with decomposition.

Found %: C 65.19; 65.29; H 8.46; 8.56

$C_{13}H_{20}O_4$ Calculated %: C 65.01; H 8.33

Anhydride of cis-Decahydro-2-methyl-1,2-naphthalenedicarboxylic Acid (XV)

1. The cis acid (XVI) (120 mg) was boiled for 90 minutes with 1.5 ml of acetyl chloride. After removal of acetyl chloride under reduced pressure, volatile impurities were removed by distillation first with benzene and then with petroleum ether under reduced pressure; after this treatment the originally liquid residue solidified. The product was 100 mg of the crystalline saturated cis anhydride (XV), which, after crystallization from petroleum

ether, had a constant melting point of 66-67°.

Found %: C 70.15; 70.12; H 8.12; 8.03

$C_{13}H_{18}O_3$ Calculated %: C 70.20; H 8.15

2. Hydrogenation of 300 mg of the liquid unsaturated cis anhydride (IV) in acetic acid over platinum oxide yielded 240 mg of a crystalline substance, m.p. 63-66°, which, after crystallization from petroleum ether, yielded the pure cis anhydride (XV) of m.p. 66-67°, identical with the product obtained in the previous experiment.

Dimethyl Ester of cis-1,2,3,5,6,7,8,8a-Octahydro-2-methyl-1,2-naphthalenedicarboxylic Acid (XVII)

A suspension of 1.0 g of the cis acid (VI) in ether was treated with an excess of an ether solution of diazomethane. The liquid reaction product remaining after removal of ether was vacuum-distilled, and yielded 800 mg of the cis diester (XVII) in the form of a thick colorless oil, which did not crystallize when allowed to stand; b.p. 162-163° (5 mm), n_D^{18} 1.4955.

Found %: C 67.69; 67.70; H 8.47; 8.53

$C_{15}H_{22}O_4$ Calculated %: C 67.69; H 8.33

Dimethyl Ester of cis-Decahydro-2-methyl-1,2-naphthalenedicarboxylic Acid (XVIII)

The cis acid (XVI) (1.7 g) was treated according to the procedure of the previous experiment with an ether solution of diazomethane, and vacuum distillation yielded 1.5 g of the cis diester (XVIII) in the form of a noncrystallizing viscous oil, b.p. 163-164° (5 mm), n_D^{15} 1.4890.

Found %: C 67.46; 67.50; H 8.98; 8.92

$C_{15}H_{24}O_4$ Calculated %: C 67.17; H 9.01

trans-1,2,3,5,6,7,8,8a-Octahydro-2-methyl-1,2-naphthalenedicarboxylic Acid (XIX)

The cis diester (XVII) (700 mg) was added to a solution of 2 g of sodium in 60 ml of absolute methanol, and the mixture was boiled for 17 hours. The methanol was distilled off under reduced pressure, and 15 ml of water was added to the residue. The solution was then boiled for five hours, after which it was evaporated down to a thick slurry in a porcelain dish on a water bath. The precipitate of salts was filtered off and dissolved in the least possible amount of water; the solution was filtered and acidified with hydrochloric acid. The precipitated oil rapidly crystallized when the mixture was stirred, and 600 mg of a substance of m.p. 195-200° was obtained. Two recrystallizations from 50% aqueous acetone yielded 400 mg of the pure trans acid (XIX), m.p. 212-213° with decomposition.

Found %: C 65.62; 65.66; H 7.64; 7.81

$C_{13}H_{18}O_4$ Calculated %: C 65.52; H 7.53

Hydrogenation of the Trans Acid (XIX)

The trans acid (XIX) (200 mg) was dissolved in glacial acetic acid (5 ml) and hydrogenated over platinum oxide, and one molecular proportion (20 ml) of hydrogen was absorbed. The catalyst was filtered off, and the solvent was removed under reduced pressure. When treated with water, the residue yielded a crystalline substance, m.p. 180-190°. Attempts to crystallize it from aqueous methanol or acetone did not result in the isolation of a pure individual product, a crystalline substance of extended melting range (180-190°) being obtained in all cases. This, however, was shown by analysis to have the composition of trans-decahydro-2-methyl-1,2-naphthalenecarboxylic acid (XX).

Found %: C 65.29; 65.27; H 8.36; 8.61

$C_{13}H_{20}O_4$ Calculated %: C 65.01; H 8.33

Dimethyl Ester of cis-1,2,3,4,5,6,7,8-Octahydro-2-methyl-1,2-naphthalenedicarboxylic Acid (XXI)

The cis diester (XVII) (950 mg) was added to 10 ml of a mixture of two parts of acetic anhydride and one part of glacial acetic acid saturated with dry hydrogen chloride, and the solution was heated at 60° for one hour. The solvents were driven off, and vacuum distillation of the residue yielded 750 mg of the cis diester (XXI), b.p. 145-146° (3 mm), n_D^{20} 1.4925.

Found %: C 67.38; 67.50; H 8.44; 8.36

$C_{15}H_{22}O_4$ Calculated %: C 67.69; H 8.33

trans-1,2,3,4,5,6,7,8-Octahydro-2-methyl-1,2-naphthalenedicarboxylic Acid (XXII)

By the procedure used for the isomerization of the cis diester (XVII), 700 mg of the cis diester (XXI) yielded 500 mg of a crystalline substance, m.p. 153-158°. Two recrystallizations (from 50% aqueous acetone and from 50% aqueous methanol) yielded the pure trans acid (XXII), having a constant m.p. of 173-174° with decomposition.

	Found%:	C 65.39; 65.49; H 7.51; 7.40
$C_{13}H_{18}O_4$	Calculated%:	C 65.52; H 7.53
	Found:	M 234.4 (by titration with NaOH)
	Calculated:	M 238.3

The trans acid (XXII) gave a positive reaction with tetranitromethane and was not hydrogenated in presence of platinum oxide under the usual conditions.

SUMMARY

1. A study has been made of the diene condensation of 1-vinylcyclohexene (I) with citraconic anhydride (II), and it has been shown that in this reaction the ortho and meta adducts (III) and (IV) are formed in the proportions of 5 : 1 and in an overall yield of 92%. Hydrolysis of the cis anhydrides (III) and (IV) yielded the corresponding cis-1,2,3,5,6,7,8,8a-octahydromethyl-1,2-naphthalenedicarboxylic acids (V) and (VI), and the structures and spatial configurations of these have been proved.

2. The unsaturated cis anhydrides (III) and (IV), and also the corresponding cis acids (V) and (VI), are readily hydrogenated in a sterically selective manner at a platinum catalyst into the corresponding saturated compounds (VII), (VIII), (XV), and (XVI), the direction of the reaction being determined by the screening effect of the cis substituents at (C-1) – (C-8a) on the double bond.

3. By the isomerization of the cis diesters (IX), (X), and (XVII) with the aid of sodium methoxide, the corresponding trans acids (XI), (XII), and XIX) have been obtained in good yield, and this reaction may provide a convenient method for their synthesis. The hydrogenation of the unsaturated trans acid (XIX), unlike that of the isomeric trans acid (XI), is not sterically selective.

4. By treatment with acetyl chloride in a mixture of acetic anhydride and acetic acid, the cis diesters (IX) and (XVII) have been caused to undergo isomerization with displacement of the double bond to give the cis diesters (XIII) and (XXI). Further isomerization of these in presence of sodium methoxide yields the trans acids (XIV) and (XXII), which have an inter-ring double bond. These acids, as also the esters (XIII) and (XXI), cannot be hydrogenated over a platinum catalyst under the usual conditions.

5. Irrespective of the temperature (within the range 100-230°), the condensation of 1-vinylcyclohexene with citraconic anhydride proceeds by exo-addition.

Received April 6, 1954

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

LITERATURE CITED

[1] I. N. Nazarov and T. D. Nagibina, J. Gen. Chem., 23, 577 (1953).*

[2] I. N. Nazarov and T. D. Nagibina, J. Gen. Chem., 18, 1090 (1948).

[3] I. N. Nazarov, I. V. Torgov, and M. V. Kuvarzina, J. Gen. Chem., 22, 220 (1952).**

[4] I. N. Nazarov and T. D. Nagibina, J. Gen. Chem., 23, 801 (1953).***

[5] I. N. Nazarov et al., Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, No. 5, 901,920,929, No. 6, 1074, 1091.****

[6] J. Heer, K. Miescher, Helv., 31, 219 (1948); W. Bachmann, J. Chemerda, J. Am. Chem. Soc., 70, 1468 (1948); W. Bachmann, J. Controulis, J. Am. Chem. Soc., 73, 2636 (1951).

---

* See Consultants Bureau Translation, p. 599.

** " " " " p. 213.

*** " " " " p. 819

**** " " " " p. 799, 817, 827; 955, 969.

[7] I. N. Nazarov and I. L. Kotlyarevsky, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, No. 6, 1100.*

[8] K. Adler, H. Vagt, W. Vogt, Ann. 565, 135 (1949), J. Meek, F. Lorenzi, S. Cristol, J. Am. Chem. Soc. 74, 2669 (1952), K. Adler, M. Schumacher, O. Wolf, Ann. 564, 79 (1949).

[9] P. Robins, J. Walker, J. Chem. Soc., 1952, 642.

[10] Organic Syntheses, Part II, Foreign Lit. Press, 1949, p. 570.

[11] I. M. Heilbron and H. M. Bunbury, Dictionary of Organic Compounds, Vol. 2, Foreign Lit. Press, 1949, p. 783.

---

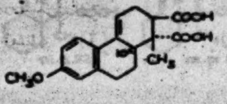
* See Consultants Bureau Translation, p. 977.

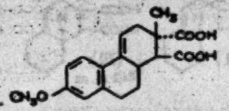
STEREOCHEMISTRY OF CYCLIC COMPOUNDS

COMMUNICATION 5. CONDENSATION OF 1-VINYLCYCLOHEXENE WITH DIMETHYL MESACONATE

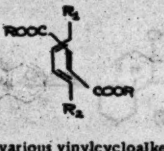
I. N. Nazarov, V. F. Kucherov, and V. M. Andreev

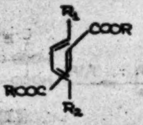
In spite of the large number of investigations devoted to the study of the diene condensation of trans dienophiles, only in isolated cases has the condensation of these with vinylcycloalkenes been investigated. The possibility of such a reaction was first noted in the case of the condensation of bicyclohexenyl with fumaric acid [1]. In 1951 Bachmann and Controulis [2] described the condensation of mesaconic acid with 1,2-dihydro-7-methoxy-4-vinylnaphthalene, which resulted in the formation of two trans structural isomers, the steric configurations of which were not proved (configuration at C-10a).





It may now be regarded as firmly established that the condensation of vinylcycloalkenes with trans dienophiles makes it possible to synthesize not only structural isomers, but also stereoisomers as has been observed on a number of occasions in the reactions of the simplest unsymmetrical dienes with certain trans dienophiles [3]. In diene condensations with trans dienophiles, the different orientations of the reactants are equally probable, so that the different stereoisomeric forms of the trans adducts can be formed:





The use in this reaction of various vinylcycloalkenes as unsymmetrical dienes can result in the formation of stereoisomeric forms of polycyclic compounds having a trans disposition of substituents.

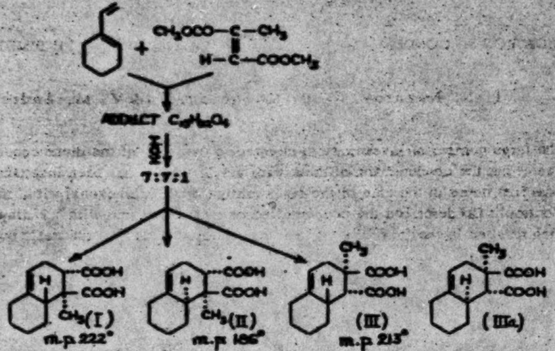
As the simplest example of a diene condensation of this type, we have studied the reaction of 1-vinylcyclohexene with dimethyl mesaconate. It was found that, when a mixture of dimethyl mesaconate and excess of 1-vinylcyclohexene (2-2.5 molecular proportions) was heated in benzene at 230-240° for four hours, a liquid adduct was formed (yield greater than 70%), a small amount of the dimer of 1-vinylcyclohexene being present as an impurity. At a lower temperature (120-140°) the reaction was much slower. Repeated vacuum fractionation yielded the pure liquid adduct, and analysis showed that it corresponded in composition to the expected condensation product $C_{15}H_{22}O_4$. In spite of its narrow boiling range, this product was not homogeneous, and its hydrolysis with 30% aqueous caustic potash, followed by fractional crystallization, yielded three individual crystalline acids (I), (II), and (III) in the proportions of 7 : 7 : 1 approximately. (See Scheme (A) on following page.)

It was not found possible to isolate the fourth possible isomer (IIIa), corresponding to the acid (III) with a different disposition of hydrogen at C-8a.

The acid (I) was found to be identical with trans-1,2,3,5,6,7,8,8a-octahydro-1-methyl-1,2-naphthalenedicarboxylic acid, which we prepared previously [4] by the isomerization of the corresponding cis diester (IV). When dehydrogenated in presence of palladized charcoal, this acid gave 1-methylnaphthalene. (See Scheme (B) on following page.)

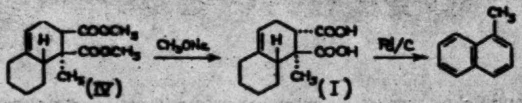
The acid (III), which was formed in small amount, was found to be identical with the trans-1,2,3,5,6,7,8,8a-octahydro-2-methyl-1,2-naphthalenedicarboxylic acid obtained by the isomerization of the cis diester (V) and

(A)



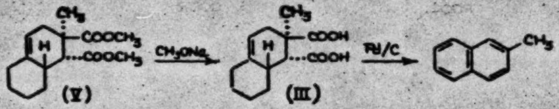
$CH_3OCO-C-CH_3$
$H-C-COOCH_3$
ADDUCT $C_{15}H_{22}O_4$
KOH
7:7:1
COOH
COOH
CH_3(I)
m.p. 222°
CH_3(II)
m.p. 186°
CH_3
(III)
m.p. 213°
(IIIa)
H

(B)



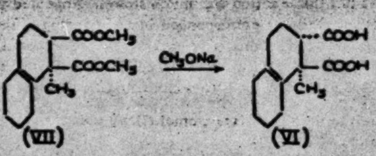
$COOCH_3$
$COOCH_3$
CH_3(IV)
CH_3ONa
COOH
COOH
CH_3(I)
Pd/C
CH_3
H

shown previously to have this structure by dehydrogenation to 2-methylnaphthalene [4].



CH_3
$COOCH_3$
$COOCH_3$
(V)
CH_3ONa
COOH
COOH
(III)
Pd/C
CH_3
H

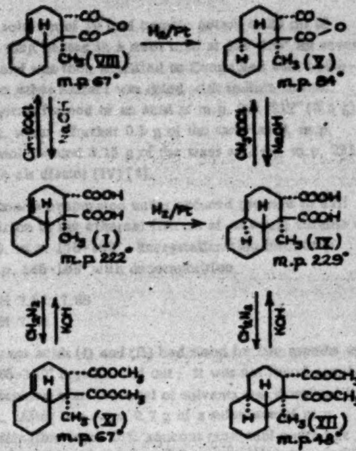
Dehydrogenation of the trans acid (II) over palladized charcoal again yielded 1-methylnaphthalene, so that its structure is similar to that of the trans acid (I). It was found, however, that the trans acid (II) was different from the trans acid (VI), which has an inter-ring double bond and has been prepared previously by us [4] by isomerization of the cis diester (VII):



$COOCH_3$
$COOCH_3$
CH_3
(VII)
CH_3ONa
COOH
COOH
CH_3
(VI)

The trans acids (I) and (II), therefore, have identical skeletons, and differ not in the position of the double bond, but only in the configuration of the hydrogen at C-8a.

We have studied some of the reactions of the three isomeric trans acids (I), (II), and (III). When the trans acid (I) was treated with acetyl chloride, it readily yielded the trans anhydride (VIII), m.p. 67°. Both the trans acid (I) itself and its anhydride (VIII) were readily hydrogenated in presence of a platinum catalyst with formation of the saturated trans acid (IX) and trans anhydride (X). The latter was formed also by the action of acetyl chloride on the saturated trans acid (IX). In this case an interesting feature of the hydrogenation was the formation of a single saturated compound. This steric selectivity in the course of the hydrogenation is most probably to be explained by the presence of powerful simultaneous screening effects of the carboxyl group at C-1 and the hydrogen at C-8a, which exceed the screening effects of the methyl group at C-1 and the carboxyl at C-2; this view is supported by an examination of Stuart atomic models. Hence, hydrogenation of the compounds (I) and (VIII) should occur trans to the hydrogen at C-8a and to the carboxyl at C-1, and the hydrogenation products (IX) and (X) should have the configuration of trans-decahydronaphthalene.

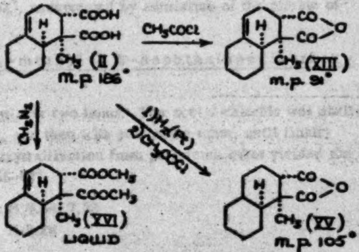


When treated with diazomethane, the trans acids (I) and (IX) give the corresponding trans diesters (XI) and (XII) in quantitative yield. The unsaturated trans diester (XI), unlike the corresponding diester of the cis series, cannot be caused to undergo isomerization in presence of acidic reagents with displacement of the double bond to the inter-ring position.

The trans acids (II) and (III) also readily give the trans anhydrides (XIII) and (XIV) under the action of acetyl chloride. In this case hydrogenation in presence of a platinum catalyst, both of the trans acids themselves and of their anhydrides, does not proceed in a selective manner, and therefore yields a mixture of isomers that is difficult to separate. Only in the case of the trans acid (II) was it found possible to isolate the individual saturated trans anhydride (XV), m.p. 105°, from the product obtained by treatment of the mixture of saturated acids with acetyl chloride, and the configuration of this at C-4a has not been established.

Atomic models of the trans acids (II) and (III) indicate that there is no preferential screening of the double bond by the substituents, and in this case hydrogenation goes in both of the possible directions.

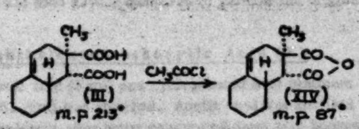
The trans acid (II) is readily converted by diazomethane into the trans diester (XVI), which, like the trans diester (XI), is not capable of isomerization with displacement of the double bond to the inter-ring position, such as occurs in the case of the corresponding esters of the cis series.



EXPERIMENTAL

Condensation of 1-Vinylcyclohexene with Dimethyl Mesaconate

A mixture of 30 g of dimethyl mesaconate (b.p. 80° (5 mm); n_D^{20} 1.4550) [5], 50 g of 1-vinylcyclohexene, and 70 ml of cryoscopic benzene was heated in presence of 0.2 g of pyrogallol in a steel tube in an atmosphere of nitrogen at 230-240° for four hours. After removal of benzene, excess of 1-vinylcyclohexene, and a small amount of dimethyl mesaconate by distillation, the reaction product was vacuum-distilled and yielded 48.9 g of a thick oil, b.p. 135-150° (3.5 mm) and n_D^{20} 1.4998. Two vacuum fractionations yielded 37.2 g of adduct, b.p. 130-134° (2 mm) and n_D^{20} 1.4960. Yield 74% on the dimethyl mesaconate.



Found %: C 67.81, 67.70; H 8.57, 8.57

$C_{22}H_{32}O_6$ Calculated %: C 67.69, H 8.33

Hydrolysis of the Condensation Product

The adduct (17.5 g; b.p. 130-134° / 2 mm) was boiled with a solution of 30 g of caustic potash in 80 ml of water until solution was complete (five hours), and the solution was then heated in a steel tube at 130-135° for seven hours. The brown solution was treated with charcoal and filtered, and was then acidified to Congo Red with hydrochloric acid. The precipitated oil was extracted with ether, and the ether extract was dried with sodium sulfate. Ether was distilled off until the volume reached 40-50 ml, when crystals formed of an acid of m.p. 211-212° (3.5 g). These were filtered off, and the filtrate was evaporated to half bulk, when a further 0.5 g of the same acid, m.p. 207-210°, was isolated. Recrystallization from 70% aqueous methanol yielded 3.15 g of the trans acid (I), m.p. 221-222°, identical with that prepared previously by isomerization of the cis diester (IV) [4].

After separation of the trans acid (I), the ethereal mother liquor was evaporated under reduced pressure to half bulk, and 1.4 g of a trans acid of m.p. 181-184° was isolated. Addition to the ethereal filtrate of an equal volume of petroleum ether resulted in the separation of 1.8 g of the same acid, m.p. 178-182°. Recrystallization from 50% aqueous acetone yielded 3.05 g of the individual trans acid (II), m.p. 185-186° with decomposition.

Found %: C 65.67; 65.48; H 7.81; 7.69

$C_{13}H_{18}O_4$. Calculated %: C 65.52 H 7.53

After the mother liquor remaining after the separation of the trans acids (I) and (II) had stood for two months at room temperature, 2.2 g of a nonhomogeneous substance of m.p. 165-180° crystallized out; it was not found possible to isolate any individual substance from this. The liquid residue obtained after removal of solvents was dissolved in 4 ml of ether and diluted with an equal volume of petroleum ether. After two days, 0.7 g of a substance of m.p. 185-195° crystallized out from the solution, and this, after recrystallization from 50% aqueous methanol melted at 200-205° (0.5 g). A second recrystallization from 50% aqueous methanol yielded 0.4 g of the crystalline trans acid (III), m.p. 210-211°, undepressed by admixture of the acid obtained previously by the isomerization of the cis diester (V) [4].

Dehydrogenation of the Trans Acid (I)

A mixture of 1.1 g of the trans acid (I), m.p. 221-222°, 0.5 g of palladized charcoal (10% Pd), and 20 ml of cryoscopic benzene was heated in an autoclave in an atmosphere of nitrogen at 360-370° for 18 hours. The catalyst was filtered off, the benzene was distilled off, and the residue was distilled under atmospheric pressure, when 0.43 g of a hydrocarbon having n_D^{20} 1.5975 was obtained. Its picrate, prepared by the usual method, melted at 139.5-141°, and the melting point was not depressed by admixture of the picrate of 1-methylnaphthalene.

Dehydrogenation of the Trans Acid (II)

When treated by the above procedure, 1.0 g of the trans acid (II) of m.p. 185-186° yielded 0.35 g of a hydrocarbon having n_D^{20} 1.6040. Its picrate had a melting point of 140-141°, undepressed by admixture of the picrate of 1-methylnaphthalene.

Anhydride of trans-1,2,3,5,6,7,8,8a-Octahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (VIII)

The trans acid (I) (0.5 g) was boiled with acetyl chloride (5 ml) for two hours. The acetyl chloride was distilled off, and the residue was repeatedly evaporated down with benzene, and then with petroleum ether, until finally 0.44 g of a crystalline substance of m.p. 63-67° was obtained. Recrystallization from petroleum ether yielded the pure trans anhydride (VIII) in the form of rhombic crystals, m.p. 66-67°.

Found %: C 70.71; 70.74; H 7.34; 7.35

$C_{13}H_{16}O_3$. Calculated %: C 70.92; H 7.28

Hydrolysis of the trans anhydride (VIII) with 10% aqueous caustic soda gave a quantitative yield of the original trans acid (I).

Anhydride of trans-Decahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (X)

The trans anhydride (VIII) (0.2 g) was dissolved in glacial acetic acid (5 ml) and hydrogenated over platinum oxide, when one molecular proportion of hydrogen (25 ml; 20°, 751 mm) was absorbed. Acetic acid was distilled off under reduced pressure, and the liquid residue crystallized completely after being evaporated down with benzene, and then with petroleum ether. Recrystallization from petroleum ether yielded 0.14 g of the pure saturated trans anhydride (X), m.p. 83.5-84.5°.

Found %: C 70.12; 69.99; H 7.95; 7.90

$C_{13}H_{18}O_3$. Calculated %: C 70,21; H 8.15

trans-Decahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (IX)

1. The trans acid (I) (0.4 g) was dissolved in glacial acetic acid (10 ml) and hydrogenated over platinum oxide, when one molecular proportion of hydrogen (50 ml: 26°, 743 mm) was absorbed in the course of three hours. Removal of solvent under reduced pressure yielded a crystalline product of m.p. 199-205°, and this, after recrystallization from 50% aqueous acetone, yielded 0.28 g of the saturated trans acid (IX), m.p. 227-228°, identical with the substance prepared previously [4].

2. The saturated trans anhydride (X) (0.35 g) was boiled with 3 ml of 5% aqueous caustic soda for ten minutes. The acid precipitated by acidification, which melted at 228-229° after crystallization from 50% aqueous acetone, was found to be identical with the trans acid (IX) obtained in the previous experiment. When boiled with acetyl chloride, the saturated trans acid (IX) readily yielded the saturated trans anhydride (X), m.p. 83-84°.

Dimethyl Ester of trans-1,2,3,5,6,7,8,8a-Octahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (XI)

A suspension of 2.6 g of the trans acid (I) in 50 ml of ether was treated with excess of an ether solution of diazomethane. After removal of ether, 2.6 g of a crystalline substance, m.p. 61-62°, was obtained. Crystallization from a small amount of petroleum ether yielded the pure trans diester (XI), having a constant melting point of 62-63°. Hydrolysis of the trans diester (XII) with 40% aqueous caustic caustic potash gave the original trans-diester (I) in good yield.

Found %: C 67.77; 67.83; H 8.44; 8.45

$C_{15}H_{22}O_4$. Calculated %: C 67.69; H 8.33

Attempt to Effect Isomerization by Double-bond Displacement in the Trans Diester (XI)

The trans diester (XI) (2.0 g; m.p. 62-63°) was added to 20 ml of a mixture of two parts of acetic anhydride and one part of glacial acetic acid saturated with dry hydrogen chloride, and the solution was heated at 60° for 90 minutes. After removal of solvents, the liquid residue was vacuum-distilled, when it yielded 1.5 g of a colorless viscous liquid, b.p. 161-162° (5 mm) and n_D^{21} 1.4970, which gradually solidified. Crystallization from petroleum ether yielded 1.3 g of a crystalline substance, m.p. 61-63°, which was found to be identical with the original trans diester (XI).

Dimethyl Ester of trans-Decahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (XII)

The saturated trans acid (IX) (0.6 g; m.p. 228-229°) was treated with excess of an ether solution of diazomethane, and the ether was distilled off. The liquid residue gradually crystallized when cooled, and after being washed on the filter with cold petroleum ether it melted at 46-48° (0.5 g). After crystallization from a small amount of petroleum ether, the saturated trans diester (XII) melted at 47-48°.

Found %: C 67.09; 67.15; H 9.02; 9.02

$C_{15}H_{24}O_4$. Calculated %: C 67.16; H 9.01

Hydrolysis of the trans diester (XII) with 40% aqueous caustic potash yielded the original trans acid (IX), m.p. 227-229°

Anhydride of trans-1,2,3,5,6,7,8,8a-Octahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (XIII)

The trans acid (II) (0.2 g; m.p. 185-186°) was boiled with 2 ml of acetyl chloride for two hours. The acetyl chloride was distilled off, and the residue was heated under reduced pressure at 80-85° for 30 minutes to remove acetic anhydride. The liquid residue crystallized when treated with petroleum ether and cooled, and 0.1 g of glistening crystals of the trans anhydride (XIII) was obtained. The melting point, after crystallization from a small amount of petroleum ether, was 90.5-91.5°

Found %: C 70.98, 70.95; H 7.27, 7.39

$C_{13}H_{16}O_3$. Calculated %: C 70.92; H 7.28.

Hydrolysis of the trans anhydride (XIII) with 3% aqueous caustic soda yielded the original trans acid (II), m.p. 185-186°.

Hydrogenation of the Trans Acid (II)

The trans acid (II) (1.7 g) was dissolved in methanol (40 ml) and hydrogenated over platinum oxide in presence of a small amount of chloroplatinic acid. Hydrogenation was slow, and one molecular proportion of hydrogen

(173 ml) was absorbed in the course of four hours. Methanol was removed under reduced pressure, and a thick oil remained. This partially solidified when carefully rubbed out with petroleum ether. The crystalline product was filtered off and washed with a mixture of diethyl ether and petroleum ether (1 : 1). The product was 1.0 g of a substance of m.p. 183-190°. After two crystallizations from 50% aqueous methanol, the saturated trans acid did not have a sharp melting point (200-203°). It was a mixture of stereoisomers, and we were unsuccessful in separating them by crystallization.

Found %: C 65.25; 65.05; H 8.34; 8.39
$C_{13}H_{20}O_4$. Calculated %: C 65.01; H 8.33

This mixture (0.45 g; m.p. 200-203°) was converted into the anhydrides by treatment at the boil with acetyl chloride. With great difficulty the liquid residue remaining after removal of acetyl chloride was induced to crystallize: it was repeatedly evaporated down with benzene and with petroleum ether. Fractional crystallization from petroleum ether yielded 0.1 g of an individual saturated trans anhydride (XV),which crystallized in the form of glistening cubes, m.p. 104-105°.

Found %: C 70.39; 70.42; H 8.31, 8.04
$C_{13}H_{18}O_3$. Calculated %: C 70.21; H 8.15

Dimethyl Ester of trans-1,2,3,5,6,7,8,8a-Octahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (XVI)

A suspension of 1.5 g of the trans acid (II), m.p. 185-186°, in ether was treated with excess of an ether solution of diazomethane. Ether was distilled off, and vacuum distillation of the residue yielded 1.4 g of the trans diester (XVI) in the form of a colorless viscous oil, b.p. 152-153° (4 mm) and n_D^{22} 1.4975.

Found %: C 67.65; 67.66; H 8.34; 8.31
$C_{15}H_{22}O_4$. Calculated %: C 67.69 H 8.33

Hydrolysis of the trans ester (XVI) with 40% aqueous caustic potash yielded the original trans acid (II), m.p. 184-185°.

Attempt to Effect Isomerization by Double-bond Displacement in the Trans Diester (XVI)

A solution of 1.2 g of the trans diester (XVI) in 12 ml of a mixture of acetic anhydride and acetic acid saturated with dry hydrogen chloride was heated at 60° for 2 hours 30 minutes. The solvents were distilled off, and vacuum distillation of the liquid residue yielded 0.95 g of a thick oil, b.p. 161-162° (6 mm) and n_D^{22} 1.4980. Hydrolysis with 40% aqueous caustic potash yielded 0.8 g of a trans acid, and crystallization of this from 70% methanol yielded 0.6 g of m.p. 185-186°; it was found to be identical with the original trans acid (II).

Anhydride of trans-1,2,3,5,6,7,8,8a-Octahydro-2-methyl-1,2-naphthalenedicarboxylic Acid (XIV)

A mixture of 0.15 g of the trans acid (III), m.p. 212-213°, and 1.5 ml of acetyl chloride was boiled for one hour. The liquid reaction product remaining after removal of acetyl chloride was heated in a vacuum at 80-85° for 30 minutes. The residue, which gradually crystallized when treated with petroleum ether, was washed on the filter with a small amount of cold petroleum ether. The product was 0.11 g of the trans anhydride (XIV), which, after crystallization from petroleum ether, melted at 86-87°.

Found %: C 70.84; 70.85; H 7.15; 7.20
$C_{13}H_{16}O_3$. Calculated %: C 70.92; H 7.28

Hydrolysis of the trans anhydride (XIV) with 3% aqueous caustic soda gave a quantitative yield of the original trans acid (III), m.p. 212-213°.

SUMMARY

1. When 1-vinylcyclohexene was condensed with dimethyl mesaconate, three isomeric trans-1,2,3,5,6,7,8,8a-octahydromethyl-1,2-naphthalenedicarboxylic acids (I), (II), and (III) were isolated in the proportions of 7 : 7 : 1. The structures and spatial configurations of these acids have been proved.

2. The trans acids (I) and (II), which were obtained in equal amount, are of ortho structure and differ from one another only in the position of the hydrogen atom at C-8a. The trans acid (III), which was obtained in small amount, is a meta isomer in which the hydrogen at C-8a is trans with respect to the carboxyl at C-1.

3. It has been shown that the hydrogenation of the trans acid (I) and of its anhydride (VIII) in presence of platinum oxide proceeds in a selective manner with formation of the individual compounds (IX) and (X), whereas the trans acids (II) and (III) are not hydrogenated selectively under these conditions, but give mixtures of stereoisomers.

4. Such sterically selective hydrogenation of 1,2,3,5,6,7,8,8a-octahydromethyl-1,2-naphthalenedicarboxylic acids and their derivatives occurs only when the 8a-hydrogen and the 1-carboxyl are arranged cis to one another; this view is supported by an examination of atomic models.

5. The trans diesters (XI) and (XVI) are unable to undergo isomerization with displacement of the double bond to the inter-ring position, such as occurs in the case of the corresponding esters of the cis series.

Received April 6, 1954

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

LITERATURE CITED

[1] F. Bergmann, H. Eschinazi, M. Neeman, J. Org. Chem., 8, 179 (1943).

[2] W. Bachmann, J. Controulis, J. Am. Chem. Soc. 73, 2636 (1951).

[3] D. Craig, J. Am. Chem. Soc., 72, 1678 (1950); K. Adler, W. Vogt, Ann. 571, 137 (1951); K. Adler, M. Schumacher, Ann., 571, 93,108, 122 (1951).

[4] I. N. Nazarov, V. F. Kucherov, and V. M. Andreev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, No. 1, 78.*

[5] G. Jeffery, A. Vogel, J. Chem. Soc., 1948, 664.

---

* See Consultants Bureau Translation, p. 67.

BLANK
PAGE

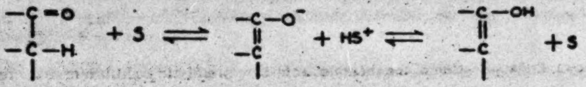
THEORY OF TAUTOMERIC EQUILIBRIUM IN SOLUTION

EFFECT OF SOLVATION ON THE EQUILIBRIUM BETWEEN THE KETO AND ISOMERIC CIS AND TRANS ENOL FORMS

M. I. Kabachnik

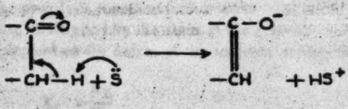
During recent years we have shown that the theory of acid-base protolytic equilibrium is applicable to prototropic tautomeric equilibrium [1]. By the use of this theory we have succeeded in deriving some important quantitative relationships characterizing keto-enol tautomeric equilibrium. These calculations were based on the concept of the ionization-protolysis mechanism of tautomeric change, which has been advanced at various times and in various forms by a number of authors, particularly Pedersen [2].

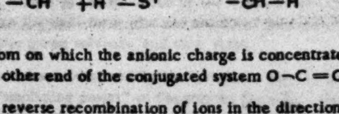
The results of numerous investigations on keto-enol tautomeric equilibrium in solution indicate that it is an acid-base equilibrium of two acids – the keto and enol forms which yield, by ionization, the same, common anions of enolate structure. Proton transfer from keto to enol and back is effected by the participation of proton-carrier molecules S, which can unite reversibly with a proton.



The part of proton carrier (S) may be played by any species having an affinity for a proton. This can be solvent molecules, if they have basic properties (water, alcohols, ethers), and solvent anions (hydroxyl anions in water, acetate anions in an acetic acid solution, which are known to have strongly basic properties); this can consist also of the molecules of any bases present in the solution (pyridine, amines, etc.). Finally, in aprotic solvents, such as benzene, carbon disulfide, and hydrocarbons, the part of proton carrier (S) may be played by the molecules of the keto-enol compound themselves, to an extent depending on their ability to unite with protons. In all cases the role of the species S is the same: to remove a proton from one place in an organic molecule (for example, from the methylene group of the keto form), and then to attach the proton to another place in the anion formed (for example, to the oxygen of the enolate ion), and vice versa.

In one of the stages of tautomeric change, the process proceeds with transfer of reaction center [3]. That is to say, in the protolysis of the keto form, the anionic charge appears not on the carbon atom from which the proton goes, but on the oxygen atom at the other end of the conjugated system H–C–C = O. Also, in the recombination of the ions with formation of the keto form:



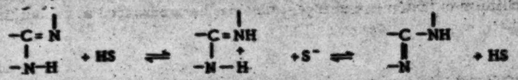


the proton unites not with the oxygen atom on which the anionic charge is concentrated (or almost entirely concentrated), but with the carbon atom at the other end of the conjugated system O–C = C.

Ionization of the enol form and the reverse recombination of ions in the direction of the enol form occur without transfer of reaction center: the ionic charge arises and subsequently disappears at the atom in the molecule from which the proton breaks away and to which it later returns. Protolysis of the enol form is rapid, whereas protolysis of the keto form (pseudoacid) is slow.

From the physicochemical point of view, keto-enol tautomeric equilibrium is a complex case of acid-base protolytic equilibrium in solution. It differs from ordinary acid-base equilibrium in two respects: in the first place, there are two acids instead of one corresponding to one sort of anions, so that the anion has two different basicity constants (for addition of the proton at two different places in the anion); and, in the second place, one of the acids taking part in the equilibrium (the keto form) is a pseudoacid, which ionizes slowly. In other respects, keto-enol tautomeric equilibrium is subject to the same laws as the ionization equilibrium of the usual weak acids.

This concept of keto-enol tautomeric equilibrium is no doubt applicable also to other forms of prototropic equilibrium in substances of an acidic character. We must point out that the formation of a pseudoacid is not an essential feature of the tautomeric equilibria of acids: in lactim-lactam tautomerism, for example, both forms are true acids. We must point out also that such concepts must be applicable also to the prototropic tautomerism of substances of a basic nature. In this case, proton transfer is accompanied by the formation not of a common anion, but of a common cation, which arises from both tautomeric forms as the result of the addition of a proton to each of them at different ends of the conjugated system of atoms. This occurs, for example, in amidine tautomerism:



It may be considered that keto-enol tautomeric changes in acid media proceed by a similar mechanism (for example, in sulfuric acid solution [4]), and that this applies in general for the acid catalysis of keto-enol changes. We consider that the laws found for keto-enol equilibrium are of a general character, and may be extended, with some modifications, to other examples of tautomerism.

As we have shown, the application of the theory of acid-base protolytic equilibrium to the ternary buffer system:

$$KH + S \rightleftharpoons E^- + HS^+ \rightleftharpoons EH + S,$$

(in which KH represents the keto form, and EH the enol form) results (for dilute solutions) in a simple relationship between the tautomeric equilibrium constant K_{TS} and the ionization or protolysis constants of the keto and enol forms, treated as acids:

$$K_{TS} = \frac{[EH]}{[KH]} = \frac{K_{KS}}{K_{ES}} = \frac{K'_{KS}}{K'_{ES}} = \frac{K_K}{K_E} \cdot \frac{f_{KS}}{f_{ES}} . \qquad (1)$$

([EH] and [KH] are the concentrations of the tautomers; K_{KS} and K_{ES} are the ionization constants of the keto and enol forms in the solvent S; K'_{KS} and K'_{ES} are the corresponding constants for protolysis by the base S; K_K and K_E are thermodynamic acidity constants; and f_{KS} and f_{ES} are activity coefficients*).

The tautomeric equilibrium constant is equal to the ratio of the ionization constants of the keto and enol forms in the given solvent (and also to the ratio of the protolysis constants); it is equal also to the ratio of the thermodynamic acidity constants of the keto and enol forms, multiplied by the ratio of the activity coefficients. The ratio of the thermodynamic acidity constants does not depend on the nature of the solvent; it may be termed the "thermodynamic constant" of tautomeric equilibrium K_t.

$$K_t = \frac{K_K}{K_E} \qquad (2)$$

It characterizes the "enolizability" of the tautomeric compound, quite apart from any effect due to the solvent. The higher the acidity constant of the keto form and the lower the acidity constant of the enol form, the higher the "enolizability" of the given tautomeric compound.

The ratio f_{KS}/f_{ES} expresses the effect of the solvent on the keto-enol tautomeric equilibrium, i.e. its "enolizing power". Here the most important factor is the nature of the solvation of the keto and enol forms by the given solvent. The higher the solvating effect of the solvent on the enol form (the undissociated molecule), the lower its activity coefficient and the greater the enolization in the given solvent; and vice versa.

In each case the position of equilibrium will be determined by both factors: the "enolizability" of the tautomeric compound, given by the value of K_t, and the "enolizing power" of the solvent f_{KS}/f_{ES}, which depends on the relative degrees of solvation of the forms. The position of tautomeric equilibrium is always found to be displaced in the direction of the form that is the less acidic in the given medium.

---

* Activities being related to a standard state that is the same for all solvents.

At very low values of K_t (acidity constant of the keto form much less than that of the enol), the substance is practically completely "ketonized" in all solvents. An example of a substance of this type is acetone ($K_{T,H_2O} = 2.5 \cdot 10^{-6}$); in aqueous solution acetone contains 0.00025% of enol form, and in hexane – the most "enolizing" solvent – the content of the enol form of acetone cannot exceed 0.06%. At very high values of K_t (acidity constant of the keto form many times as great as that of the enol form), the substance consists of almost 100% enol in all solvents. An example of substances of this second type is dimedone, which is practically completely enolized.

At intermediate values of K_t the position of tautomeric equilibrium is extremely dependent on the nature of the solvent, which displaces equilibrium in the direction of the most readily solvated form. When $K_t = 1$, i.e. when $K_K = K_E$, the position of equilibrium is entirely determined by the relative degrees of solvation of the forms. When solvents are arranged in a series according to the enolizing abilities (which corresponds only approximately with the series arranged according to the value of the dielectric constant), it is found that, in the more polar solvents the less solvated enol forms are stronger acids than the corresponding keto forms; the values of the equilibrium constant K_{TS} are correspondingly low. As we pass to the less polar solvents, which solvate the enol forms more strongly, this difference is first eliminated (the equilibrium constant passes through unity: $K_{KS} = K_{ES}$), and then the keto forms become the stronger acids ($K_{TS} > 1$). The table gives Meyer's results [5], which illustrate this behavior.

In the table, the bold stepped line separates the region in which the enol forms are more acid than the keto forms (upper left part of the table) from that in which the keto forms are more acid than the enol forms (lower right part of the table).

The effect of the solvent on the position of keto-enol tautomeric equilibrium can be treated quantitatively. Thus, the application to keto-enol equilibrium, as an equilibrium of the protolytic acid-base type, of the well-known Brönsted formula [6]

$$pK_{AS_1} = pK_{AS_2} + \text{const}^*, \tag{3}$$

together with the rules formulated by Izmailov [7], results in the important relationship

$$pK_{TS_1} = pK_{TS_2} + \text{const}', \tag{4}$$

which is valid for all keto-enol tautomeric substances in any two solvents S_1 and S_2, and which has been well confirmed experimentally. It follows from this formula that the value of f_{KS}/f_{ES}, which characterizes the enolizing power of the solvent, is constant for all keto-enol tautomeric substances. This constant is characteristic for each solvent with respect to a given class of tautomeric substances (in the case under examination – the keto-enol class).

Equation 4, after some simple transformations [8], yields the equation due to Meyer

$$K_{TS} = \mathcal{E} \cdot \mathcal{L}, \tag{5}$$

which he deduced by an empirical method [9].

According to Meyer, a measure of the enolizability of a keto-enol compound is afforded by the value of $\mathcal{E}$, which is equal to the ratio of the equilibrium constant of the given keto-enol compound to that of acetoacetic ester in the same solvent. The value of $\mathcal{L}$ is a measure of the enolizing power of the solvent; it is equal to the equilibrium constant of acetoacetic ester in the given solvent. It can be shown that the constant $\mathcal{E}$ in Meyer's equation is equal to the ratio of the thermodynamic equilibrium constants of the given keto-enol compound (K_t) and acetoacetic ester (K_t°).

$$\mathcal{E} = K_t / K_t^\circ \tag{6}$$

This quantity, of course, does not depend on the nature of the solvent. Meyer's constant $\mathcal{L}$ is also readily expressed in terms of the physicochemical constants of the keto and enol forms in the given solvent:

$$\mathcal{L} = K_t^\circ \cdot \frac{f_{KS}}{f_{ES}}$$

Hence, the constants in Meyer's equation differ from those in Equation 1 by the presence of the constant factor K_t°.

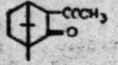
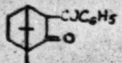
Experiment confirms these ideas. The keto and enol forms, being acids, may be titrated in solution, e.g. potentiometrically; and their ionization constants can therefore be determined. An investigation carried out by Kabachnik and Ioffe [10] has confirmed the applicability of Brönsted's formula (Equation 3) to the keto and enol forms, regarded as acids. The empirical ionization constants were determined potentiometrically with the aid of a glass electrode

---

[*] $pK = -\log K$.

TABLE

Values of K_{TS} for Some Keto-Enol Tautomeric Substances (Meyer [5])

Solvent / Substance	H_2O	$HCOOH$	67% CH_3OH	CH_3COOH	CH_3OH	CH_3COCH_3	$CHCl_3$	C_2H_5OH	$CH_3COOC_2H_5$	C_6H_6	$C_6H_5CH_3$	$(C_2H_5)_2O$	CS_2	C_6H_{14}
$CH_3COCH_2COOC_2H_5$	0.004	0.011	0.023	0.061	0.074	0.08	0.089	0.13	0.15	0.22	0.26	0.43	0.73	1.00
$CH_3COCH_2CONHC_6H_5$	–	–	0.026	0.076	0.09	–	0.09	0.18	0.33	0.15	0.19	0.80	–	–
$C_6H_5COCH_2COOCH_3$	0.008	0.028	0.046	0.16	0.16	0.18	0.18	0.32	0.33	0.45	0.62	0.90	1.6	2.2
	–	0.15	0.25	0.50	0.55	–	–	0.92	0.95	–	–	2.6	–	–
	–	–	–	–	0.87	0.85	–	1.7	2.0	–	–	6.5	–	–
$CH_3COCH_2COCH_3$	0.22	–	0.90	2.8	2.6	2.2	3.8	4.0	3.1	5.7	7.0	16	15	12
$C_6H_5COCH_2COCH_3$	–	2.3	2.5	8	9	10	13	14	–	–	–	–	–	–
$(C_6H_5CO)_2CHCOCH_3$	–	–	–	6	6	–	–	10	–	–	30	–	–	–
$C_6H_5COCH_2COC_6H_5$	–	4	–	24	22	–	–	40	–	–	–	–	–	–

for a number of equilibrium keto-enol substances ($K_{KE,S}$) dissolved in water and in 70% dioxane. These empirical ionization constants are related to the corresponding constants of the pure forms by the equation

$$K_{KE,S} = \frac{K_{KS}K_{ES}}{K_{KS} + K_{ES}}. \tag{8}$$

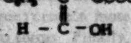
The equilibrium constants K_{TS} were then determined bromometrically by the Meyer-Dieckmann method, and the ionization constants of the separate forms were calculated from these tautomeric equilibrium constants (K_{TS}) and the empirical ionization constants for the equilibrium mixture ($K_{KE,S}$) by the equations:

$$K_{KS} = K_{KE,S}\,(K_{TS} + 1); \qquad (9) \qquad\qquad K_{ES} = K_{KE,S}\,\frac{K_{TS} + 1}{K_{TS}}. \qquad (10)$$

It was found that in aqueous solution the enol forms were generally stronger acids than the keto forms. In 70% aqueous dioxane, however, the position was often the reverse; thus, in this solvent the keto form of benzoylacetone (1-phenyl-1,3-butanedione; $K_{KS} = 1.3 \cdot 10^{-10}$) is more acid than the enol form ($K_{ES} = 3.05 \cdot 10^{-11}$). The pK_{AS} values of keto and enol forms in water and aqueous dioxane are in good accord with the linear relationship required by Equation 3.

The empirical acidity of the solution is mainly determined by the less acid form, and the position of equilibrium by the ratio of the ionization constants of the two forms. In this way the question that has long troubled chemists – the connection between the acidity of solutions of keto-enol tautomeric substances, their enolizability, and the solvation of the tautomeric forms – is now resolved.

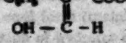
The above-cited calculations on tautomeric equilibrium, however, can characterize it only to the first approximation. In these calculations the equilibrium is considered without taking into account the possibility of cis-trans isomerism in the enol form, although such isomerism actually occurs. In some cases – in the case of phenylmalonaldehydic ester, for example – it has been found possible to effect the separation of the two stereoisomeric forms of the enol (I and II) [11]; the cis form (α - form) is characterized by the ability to give a color with ferric chloride and to form a characteristic copper complex: the trans form (γ - form) does not possess this ability; both forms readily react with bromine, which indicates that they are both enols:



$$\begin{array}{c} C_6H_5-C-COOC_2H_5 \\ \| \\ H-C-OH \end{array}$$

(I)

α - ester (liquid)

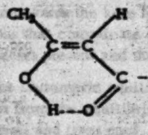


$$\begin{array}{c} C_6H_5-C-COOC_2H_5 \\ \| \\ OH-C-H \end{array}$$

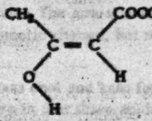
(II)

γ - ester (m.p. 110°)

According to Sidgwick [12], there is every reason to suppose that the well known enol form of acetoacetic ester of b.p. 33° (2 mm) is the cis form (III), and not the trans form (IV), its structure being characterized by the presence of an intramolecular hydrogen bond:



(III)



(IV)

Being an internal-complex compound, the cis enol form of acetoacetic ester has a lower boiling point (the keto form boils at 40-41° at 2 mm) and lower water-solubility (about 20 times as low) than the keto form; its Raman spectrum [13] is characteristic for a compound having an intramolecular hydrogen bond. Equilibrium acetoacetic ester contains not only the cis enol, but also some trans enol form [14]. The existence of enol forms in the trans configuration has been established by Henecka in a number of cases by a method depending on the inability of these enol forms to give a ferric chloride reaction [15]

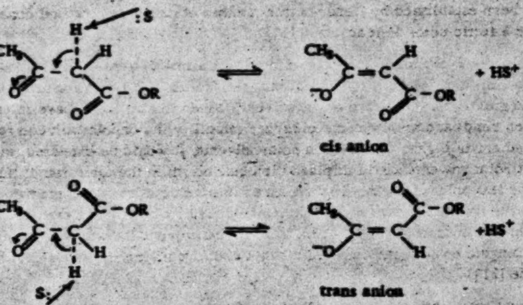
There is therefore every reason to suppose that in solutions of keto-enol tautomeric substances three forms are present in equilibrium: the keto, cis enol, and trans enol forms. The equilibrium between the cis and trans enol forms must depend greatly on the nature of the solvent. Since the cis forms have internal-complex structures (intramolecular hydrogen bond) and are therefore of higher solubility in nonpolar solvents, and the trans forms have free hydroxyl groups and are of higher solubility in polar solvents, it would be expected, in accordance with the Van't Hoff-Dimroth rule, that polar solvents would displace the equilibrium in the direction of the trans form, and nonpolar in the direction of the less polar cis form. In those cases in which cis-trans isomers have been isolated, this has been found to be true: the trans enol form of phenylmalonaldehydic ester, which crystallizes from aqueous solution, rearranges into the cis form when transferred to a hydrophobic solvent (hexane, carbon disulfide [11, 16]). A solution of phenylmalonaldehydic ester in methanol or ethanol contains mainly the trans enol form, since it gives no reaction with ferric chloride [11].

When, however, equilibrium between all of the three forms is examined (keto, cis enol, and trans enol), the relationship becomes less clear. As was pointed out for the first time by Arndt, Loewe, and Ginkök [17], it would be expected that nonpolar solvents would displace the equilibrium in the direction of the least polar form, which is readily solvated by hydrophobic solvents, i.e. in the direction of the cis enol form; this is actually observed. Polar solvents, however, should, according to these authors, displace the equilibrium in the direction of the form that is most readily solvated by polar solvents, i.e. in the direction of the trans enol form. In actual fact polar solvents displace the equilibrium in the direction of the keto form. The question "why not the trans enol ?" was examined thoroughly by these authors. They consider that the contradiction can be resolved by assuming that the keto forms can be hydrated in an aqueous medium with formation of hydrates (methylene glycols) and can be similarly converted into hemiacetals in an alcoholic medium. These hydrates and hemiacetals can be formed also from enol forms by addition of water and of alcohols. The hydrate and hemiacetal forms of the keto compounds should be more readily solvated by polar solvents than the trans enol forms, so that polar solvents will displace the equilibrium not towards the trans enol forms, but towards the hydrate of hemiacetal keto form. The authors found confirmation for this supposition in the fact that the hydrates of some keto forms are stable and isolable; thus the methyl hemiacetal of phenylmalonaldehydic ester is known [18].

It is, however, difficult to agree with the explanation of Arndt, Loewe, and Ginkök In the first place, displacement of equilibrium towards the keto form can be brought about not only by water and alcohols, but also by other polar solvents. As will be seen from the table, for any keto-enol tautomeric substance the content of keto form is greater in acetone solution than in ethanol solution. This fact is difficult to reconcile with the hypothesis of the formation of hydrates or hemiacetals. In the second place, it is important to note that it is in just those cases in which hydrate or hemiacetal formation actually does occur that departures from Meyer's rule [19] are observed, whereas Arndt and coworkers invoke the formation of hydrates or hemiacetals in order to explain the observance of this rule. We will further cite the just remarks of Briegleb and Strohmeyer [20], who pointed out that the views of Arndt and coworkers are in conflict with the fact that many keto-enol tautomeric substances (not only cyclic, but also straight-chain compounds such as malonaldehyde) contain more than 90% of enol form (mainly trans) in aqueous solution, and so do not form hydrates of the keto forms. Finally, if the formation of hydrates of the keto forms, in equilibrium with the enol forms, really does determine the displacement of equilibrium towards the keto forms in aqueous and alcoholic media, then increase in pressure should produce a still greater displacement of the equilibrium towards the hydrated keto forms (i.e. a reduction in the total number of molecules). However, according to the work of Kabachnik, Yakushkina, and Kislyakova [21], increase in pressure to 3000 atm results in only a slight displacement of the equilibrium, this displacement, however, being in the direction of the enol (mainly trans enol) forms.

It follows from these considerations that hydrate or hemiacetal formation is not the cause of the displacement of tautomeric equilibrium towards the keto forms in polar solvents. The actual causes of this phenomenon must be sought not in side reactions that complicate the process of tautomeric change, but in the process itself, in its relation to the solvation of the species present and their ionization.

We consider that the tautomeric equilibrium of cis and trans enol and keto forms is again an acid-base protolytic equilibrium; it differs from the equilibrium considered above in that three acids, not two (keto and enol) are in equilibrium: keto, cis enol, and trans enol, the cis-trans conversion of the enol form being effected through the keto form. If we examine the process of removing a proton from the keto form by means of the protophilic species S, it is found that, depending on the spatial disposition of the two carbonyls of the keto form of a 1,3-dicarbonyl compound (taken up in the course of free or restricted rotation about a C—C bond), the structure of the anion formed may be either cis or trans:



The complex acid-base equilibrium in the solution of the keto-enol compound may be represented schematically as

$$E_CH + S \rightleftharpoons E_C^- + HS^+ \rightleftharpoons KH + S \rightleftharpoons E_T^- + HS^+ \rightleftharpoons E_TH + S$$

(E_CH and E_TH are the cis and trans enols, and E_C^- and E_T^- are the corresponding anions). Following Brönsted, we may write for the ionization constants of the enol forms:

$$K_{E_C S} = \frac{[E_C^-](HS^+)}{[E_CH]} = \frac{(E_C^-)(HS^+)}{(E_CH)} \frac{f_{E_C S}}{f_{E_C^- S}} = K_{E_C} \frac{f_{E_C S}}{f_{E_C^- S}} \tag{11}$$

$$K_{E_T S} = \frac{[E_T^-](HS^+)}{[E_TH]} = \frac{(E_C^-)(HS^+)}{(E_TH)} \frac{f_{E_T S}}{f_{E_T^- S}} = K_{E_T} \frac{f_{E_T S}}{f_{E_T^- S}} \tag{12}$$

(the parentheses indicate activity and the brackets concentration). For the keto form we may write two ionization constants — for formation of the cis anion, and for formation of the trans anion:

$$K_{K_C S} = \frac{[E_C^-]\,(HS^+)}{[KH]} = \frac{(E_C^-)\,(HS^+)}{(KH)}\;\frac{f_{KS}}{f_{E_C^- S}} = K_{K_C}\,\frac{f_{KS}}{f_{E_C^- S}} \tag{13}$$

$$K_{K_T S} = \frac{[E_T^-]\,(HS^+)}{[KH]} = \frac{(E_T^-)\,(HS^+)}{[KH]}\;\frac{f_{KS}}{f_{E_T^- S}} = K_{K_T}\;\frac{f_{KS}}{f_{E_T^- S}} \tag{14}$$

From which it follows that

$$K_{TS} = \frac{[E_T H]}{[E_C H]}\;\frac{K_{E_C S} K_{K_T S}}{K_{E_T S} K_{K_S S}} = \frac{K_{E_C} K_{K_T}}{K_{E_T} K_{K_C}}\;\frac{f_{E_C S}}{f_{E_T S}} \tag{15}$$

The constant for the tautomeric cis-trans enol equilibrium depends not only on the ionization constants of these forms, but also on the ratio of the ionization constants of the keto form for cis- and trans-anion formation. Here again the equilibrium constant is defined as the product of two factors: the "thermodynamic equilibrium constant"

$$K_T = \frac{K_{E_C} K_{K_T}}{K_{E_T} K_{K_C}} \tag{16}$$

which does not depend on the nature of the solvent, and the solvation factor $f_{E_C S} / f_{E_T S}$.

The effect of the thermodynamic equilibrium constant is such that the higher the relative value of the acidity constant of the trans enol and the lower the acidity constant of the keto form for trans-anion formation, the more will the equilibrium be displaced towards the cis enol form; and vice versa.

The position of the equilibrium of cis and trans enol forms is determined by the simultaneous action of both factors

$$K_{TS} = K\,\frac{f_{E_C S}}{f_{E_T S}} \tag{17}$$

We may point out that the activity coefficient of the keto form does not enter into the expression for the constant K_{TS}; in other words, the ratio of the concentrations of the cis and trans enol forms in any solvent is independent of the solvation of the keto form by that solvent, but depends on the relative degrees of solvation of the cis and trans enol forms themselves.

The experimental (bromometric) determination of the content of enol form in solution gives the sum of the concentrations of cis and trans enol forms, and the empirical constant for keto-enol tautomeric equilibrium is

$$K_{TS} = \frac{[E_C H] + [E_T H]}{[KH]} \tag{18}$$

It is easy to show that for this constant

$$K_{TS} = \frac{K_C^S}{K_{E_C}^S} \quad \frac{K_T^S}{K_{E_T}^S} \tag{19}$$

If one of the forms, e.g. the trans enol form, has an ionization constant that greatly exceeds those of the two other forms, then the term containing this ionization constant in the denominator can be neglected, and the equilibrium constant is determined by the ratio of the ionization constants of the keto and second enol (cis) forms, i.e. by Equation 1.

The concepts developed above enable us to understand the relationships found by experiment. Let us take acetoacetic ester and acetylacetone (2,4-pentanedione) as examples. It must be supposed that the trans enol forms of acetoacetic ester and acetylacetone are stronger acids than the cis enol forms. They should be characterized by higher thermodynamic acidity constants and a greater tendency to be solvated by polar solvents. The cis enol forms are weaker acids; they are less readily solvated by polar solvents than by nonpolar solvents. This results from the presence in the cis enol forms of intramolecular hydrogen bonds, which stabilize the undissociated molecules and give them the properties of internal-complex compounds, which are more readily solvated by nonpolar solvents.

Experiments described in a paper by Eistert, Arndt, Loewe, and Ayca [22] confirm these views: in ether solution, containing mainly the cis enol form, acetylacetone is methylated only very slowly with diazomethane with formation of the ether of the cis enol; in methanol solution, in which much of the trans enol form should be present, acetylacetone reacts rapidly with diazomethane with formation of a mixture of cis and trans ethers.

As regards the keto form, in the case of acetoacetic ester the keto form is a weaker acid than the enol in all solvents except hexane. In the case of acetylacetone, this is true only for solutions in water and other strongly polar solvents. Already in a methanol medium, the keto form is found to be a stronger acid than the enol forms (or at least the cis enol form) (see the table). The keto forms are solvated more readily by polar than by nonpolar solvents, although they are solvated fairly well by the latter – they are not worse than the cis enol forms in this respect. This view finds support in the fact that for acetoacetic ester the content of keto form in almost all solvents is higher than in the vapor phase [according to Briegleb and Strohmeyer [20], at 20° the gas phase contains 48.0% of the keto form of acetoacetic ester ($K_T = 1.1$)]; and for acetylacetone in all solvents from water to toluene (see table) the content of keto form is higher than in the gas phase [according to Briegleb and Strohmeyer, at 20° the gas phase contains 6.3% of the keto form ($K_T = 14.9$)], and only in ether and carbon disulfide solutions is the content of keto form approximately the same as in the gas phase.

Whatever the solvent may be, there can be little trans enol form present at equilibrium (since its thermodynamic acidity constant is high). In nonpolar solvents the equilibrium should be displaced towards the cis enol form: it is solvated more readily in these media, and the difference in acidic properties between it and the keto form disappears in the case of acetoacetic ester, and is reversed in direction in the case of acetylacetone. This displacement of equilibrium in nonpolar solvents in the direction of the cis enol form is indeed observed experimentally. In polar solvents the equilibrium should be displaced towards the trans enol and keto forms, as being more readily solvated. Owing to its high thermodynamic acidity constant, the trans enol form will be present in low equilibrium concentration; the solution will contain mainly the keto form. The enol fraction of the solution, however, must be greatly enriched in trans form. The experimental facts are in accord with this view. An equilibrium aqueous solution of acetoacetic ester contains 0.4% of the enol form, but it does not immediately give the ferric chloride reaction that is characteristic of the cis form, but only after some time, which will permit tautomeric change to occur. This 0.4%, therefore, consists mainly of trans form.

Increase in pressure should displace the equilibrium towards the most solvated form. In aqueous solution (and in other polar solvents) this is the trans enol form. Actually, according to our results, as the pressure is raised the content of the enol form (trans!) in aqueous solution increases (to 1.63% [21]). In chloroform and toluene solutions the most solvated form is the keto form. Increase in pressure, therefore, should displace the equilibrium in these solutions towards the keto form. Experiment shows that, when a pressure of 3000 atm is applied, the contents of enol form fall from 9 and 25 to 7 and 22%, respectively.

Hence, on the basis of the treatment of tautomeric equilibrium as protolytic acid-base equilibrium, a satisfactory explanation can be given of the experimentally observed relationships between the keto and cis and trans enol forms. This concept of tautomeric equilibrium can serve as a basis for further investigations.

SUMMARY

1. Keto-enol tautomeric equilibrium in solution has been examined from the point of view of the theory of protolytic acid-base equilibrium.

2. It has been shown that in solutions of open-chain keto-enol tautomeric substances three acids participate in the equilibrium: the keto form, the cis enol form, and the trans enol form. There are two anions corresponding to these three acids: the cis enolate and the trans enolate.

3. On the basis of the theory of acid-base equilibrium, an explanation has been advanced for the properties of such solutions.

Received March 13, 1954

N. D. Zelinsky Institute of Organic Chemistry and
Institute of Heteroorganic Compounds of the
USSR Academy of Sciences

LITERATURE CITED

[1] M. I. Kabachnik, Proc. Acad. Sci. USSR, 83, 407 (1952).

[2] K. J. Pedersen, J. Phys. Chem. 37, 751 (1933); 38, 581, 593, 601 (1934).

[3] A. N. Nesmeyanov, Sci. Mem. Moscow State Univ., 132, 5 (1950).

[4] G. Schwarzenbach, Ch. Wittwer, Helv. 30, 659 (1947).

[5] K. H. Meyer, Ber. 45, 2846 (1912).

[6] J. N. Brönsted, Z. phys. Chem. A 169, 32 (1934).

[7] N. A. Izmailov, J. Phys. Chem., 24, 321 (1950).

[8] M. I. Kabachnik, Proc. Acad. Sci. USSR, 83, 859 (1952).

[9] K. H. Meyer, Ber. 47, 826 (1914).

[10] M. I. Kabachnik and S. T. Ioffe, Proc. Acad. Sci. USSR, 91, 833 (1953).

[11] W. Wislicenus, Ann. 413, 222 (1917); W. Dieckmann, Ber. 50, 1375 (1917).

[12] N. V. Sidgwick, J. chem. Soc. 127, 907 (1925); P. Nachod, Z. phys. Chem. A182, 208 (1938).

[13] K. W. F. Kohlrausch, W. Pongratz, Ber. 67, 1473 (1934).

[14] L. Knorr, Ber. 44, 1154 (1911).

[15] H. Henecka, Ber. 81, 192 (1948).

[16] H. Kaufmann, Ber. 58, 219 (1925).

[17] F. Arndt, L. Loewe, R. Ginkök Rev. Fac. Sci. Istanbul (A) 11, 147 (1946).

[18] W. Wislicenus, Ann. 413, 21 (1917).

[19] W. Dieckmann, Ber. 50, 1376 (1917).

[20] G. Briegleb, W. Strohmeyer, Angew Chem. 64, 409 (1952).

[21] M. I. Kabachnik, S. E. Yakushkina, and N. V. Kislyakova, Proc. Acad. Sci. USSR, 96, 1169 (1954).

[22] B. Eistert, F. Arndt, L. Loewe, E. Ayca, Ber. 84, 156 (1951).

BLANK
PAGE

HIGH-TEMPERATURE CONTACT-CATALYSIS REACTIONS OF BENZENE AND ITS CLOSEST HOMOLOGS IN PRESENCE OF HYDROGEN AT HIGH PRESSURE

N. I. Shuikin and N. G. Berdnikova

A number of investigations [1, 2, 3, 4] have been devoted to the study of the behavior of aromatic hydrocarbons in presence of various catalysts at high temperatures. Great interest is presented by investigations directed to the study of alkylation and dealkylation reactions of aromatic hydrocarbons [5, 6, 7, 8].

As is well known, benzene and its closest homologs possess high thermal stability. Even under severe thermal conditions, the main process is the elimination of alkyl groups as the corresponding alkenes [1, 2, 3].

When hydrogen is present under high pressure (140-200 atm), benzene homologs undergo reaction in two main directions at 440-480°: hydrogenation to the corresponding cycloalkanes, and hydrogenolysis with elimination of side chains. Under destructive hydrogenation conditions, toluene loses its CH_3 group already at 460°. Thus, according to Hofmann and Lang's results [9], at 470° toluene yields 28% of benzene. By the hydrogenation of toluene at 490°, Laider and Szayne [10] obtained 25% of benzene. Prokonets, Filaretov, and Bogoslavskaya [11] submitted benzene to destructive hydrogenation in presence of MoS_2 and hydrogen at 200 atm and at 400-470°; in the catalyzate they found methylcyclopentane, cyclohexane, and branched-chain alkanes. Similar results were obtained also by Puchkov [12] in experiments on the destructive hydrogenation of benzene in presence of hydrogen at 140 atm. Maslyansky [13] studied the reactions of benzene in presence of MoS_2 and hydrogen at 200 atm at a temperature of 500-550°, and his catalyzate contained cyclohexane, methylcyclohexane, cyclopentane, and branched alkanes (pentane and hexane isomers).

The reactions of cumene at 459° in presence of a metal oxide catalyst and hydrogen at 35 atm have been studied by Haensel and Donaldson [14]. In the catalyzate they found 1.2% of toluene, 19% of benzene, 0.9% of xylenes, and 12.3% of cycloalkanes. Among the various reactions occurring in this process, hydrogenolysis of the side chain with formation of benzene and propane predominated.

In previous papers [15, 16] we have described the results of investigations of the high-temperature contact-catalysis reactions of individual cycloalkanes and alkanes in presence of hydrogen at high pressure. On the basis of these experimental results, we have advanced hypotheses concerning the nature and direction of the reactions occurring in presence of hydrogen at high pressure and in contact with platinized aluminum oxide.

With a view to the further development of these studies, and also in order to elucidate certain peculiarities in the transformations of individual hydrocarbons, we considered it desirable to make a more detailed study of the behavior of aromatic hydrocarbons under our selected conditions. In the present investigation we have treated benzene, toluene, and ethylbenzene in presence of platinized aluminum oxide (4.5% Pt) under 20 atm of hydrogen at 460° at a space velocity of 0.43 liter/liter · hr, the molar ratio of hydrogen to hydrocarbon being 5:1.

EXPERIMENTAL

The properties of the original hydrocarbons, which were carefully purified and distilled over sodium through a column having an efficiency of about 100 theoretical plates, are given in Table 1.

TABLE 1

Properties of the Original Aromatic Hydrocarbons

Hydrocarbon	B. p. (corrected; °C)	n_D^{20}	d_4^{20}
Benzene	80.1	1.5010	0.8785
Toluene	110.5	1.4962	0.8668
Ethylbenzene	136-136.5	1.4960	0.8675

The experiments with these hydrocarbons were carried out in an apparatus of the continuous-flow type. The adjustment of the apparatus, the experimental procedure, and the analysis of the reaction products have been described previously [15,16]. In order that the investigation of the components of the catalyzate might be as complete and reliable as possible, we took 850 g of each hydrocarbon.

Caralytic Treatment of Benzene

Benzene was brought into contact with platinized alumina at 460° at a space velocity of 0.43 liter/liter· hr. in presence of hydrogen at a pressure of 20 atm. A yield of 835.6 g (98.3%) of catalyzate was obtained (n_D^{20} 1.4980; d_4^{20} 0.8661). The fractionation of 800 g of this catalyzate was carried out at 756 mm through a 100-plate column, and the results are given in Table 2.

TABLE 2

Fractional Composition of the Benzene Catalyzate

Fraction No.	Boiling range of fraction (°C)	Amount of catalyzate	n_D^{20}	d_4^{20}	Yield (% on amount of catalyzate taken for fractionation)
I	27.5 - 29.3	2.5	1.3545	0.6207	0.3
II	29.3 - 36.5	3.4	1.3575	0.6263	0.42
III	36.5 - 50.5	5.2	1.3985	0.7448	0.65
IV	50.5 - 79.5	5.3	1.4720	0.7989	0.66
V	79.5 - 80.5	774.9	1.5010	0.8788	96.8
VI	80.5-110.5	–	1.4980	–	–
VII	110.5-111.0	1.56	1.4965	0.8664	0.2
VIII	111.0-150.0	2.4	1.4960	0.8571	0.30
	Residue	5.3	1.5235	–	0.66

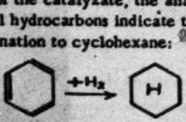
As will be seen from the results in Table 2, Fractions I and II consisted, according to their properties, of isopentane and pentane [17] respectively. Fraction III was investigated with the aid of Raman spectra, and the results showed that the principal components of this fraction were pentane (20%), cyclopentane (75%), and a small amount of methylcyclopentane. Fraction IV, boiling range 50.5 - 79.5°, was submitted to chromatographic adsorption on silica gel, which yielded 4.2 ml of benzene and 2.4 ml of naphthenes and paraffins having n_D^{20} 1.4140 and d_4^{20} 0.7478. Optical (Raman) analysis showed the presence of methylcyclopentane (75%), branched hexanes (15%), and cyclohexane (qualitatively). The properties of Fractions V and VII indicated that they consisted of benzene and toluene respectively. Fraction VIII (2.4 g) was submitted to Ullmann permanganate oxidation [18], and from the mixture of acids obtained the following acids were isolated by the procedure developed by Moldavsky and coworkers [19]: benzoic acid (m.p. 121°), phthalic acid (0.5 g, m.p. 190°), isophthalic acid (1.67 g), and terephthalic acid (0.61 g). The last two acids were converted into their methyl esters, which melted at 65° and 140° respectively. The residue (6.2 g) was fractionated from a Favorsky flask at 754 mm, and yielded:

Fraction I	B. p.	150 - 195°;	0.7 g;	n_D^{20} 1.4980;	d_4^{20} 0.8540
Fraction II	B. p.	195 - 210°;	2.1 g;	n_D^{20} 1.5185	–
Fraction III	B. p.	210 - 230°;	3.0 g;	n_D^{20} 1.5295	–

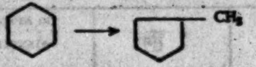
Residue and losses 0.4 g

Fraction I (b.p. 150-195°) was not investigated further owing to the inadequate amount of material available. Part of Fraction II (b.p. 195-210°) (1 g) was heated with picric acid in a water bath, when 0.6 g of a picrate of m.p. 148.5° was obtained, which indicates the presence of naphthalene in this fraction. Fraction III (b.p. 210-230°) solidified to a crystalline mass when cool; white crystalline plates, m.p. 81°, were obtained from this substance by sublimation, and judging from its properties, the substance was biphenyl.

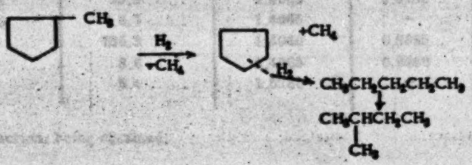
The results of the fractionation of the catalyzate, the analysis of the fractions, and comparison of the properties of the fractions with those of individual hydrocarbons indicate that in the catalytic treatment of benzene under our conditions it undergoes partial hydrogenation to cyclohexane:



which is almost completely isomerized in presence of the catalyst into methylcyclopentane:

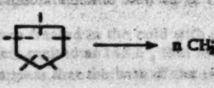


Hydrogenolysis of the methyl group of methylcyclopentane results in the formation of cyclopentane, and part of this is converted into pentane by opening of the ring. The pentane is then partially isomerized to isopentane:



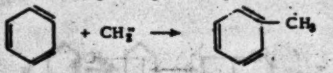
Part of the methylcyclopentane undergoes direct hydrogenolysis at various points in the ring, with formation of hexane isomers.

It is probable that in addition to these reactions there occurs also the breakdown of cycloalkanes, in particular cyclopentane, into methylene radicals



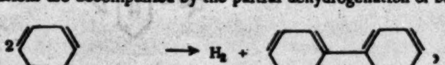
part of which is hydrogenated to methane, the other part being concerned in the methylation of benzene to toluene and xylenes:

$$CH_2^{\cdot\cdot} + H_2 \rightarrow CH_4;$$



$$C_6H_5CH_3 + CH_2^{\cdot\cdot} \rightarrow C_6H_4(CH_3)_2$$

These transformations are accompanied by the partial dehydrogenation of benzene, with formation of biphenyl



and also by the synthesis of naphthalene, the mechanism of which cannot at present be explained.

Catalytic Treatment of Toluene

Toluene was passed over the same catalyst under the same conditions, and a yield of 832.8 g (98%) of liquid catalyzate (n_D^{20} 1.4950; d_4^{20} 0.8603) was obtained. As before, 800 g of catalyzate was taken for investigation, and its fractionation was carried out through the same 100-plate column at 740 mm. The results of the analytical fractionation are given in Table 3.

As will be seen from Table 3, the properties of Fractions I and II are close to those for isopentane and pentane [17]. Fraction III (37.5-78.5°) was subjected to chromatographic adsorption, and 1.3 g of naphthenes and paraffins and 1.9 g of benzene were isolated. The naphthene-paraffin part of Fraction III was not investigated in detail owing to the inadequate amount of material available; only its specific gravity (d_4^{20} 0.6973), refractive index (n_D^{20} 1.3970), and aniline point (41.5°) were determined, but these are sufficient to indicate that it contained not only cycloalkanes, but also alkanes, which probably arose by the hydrogenolysis of mono- and di-substituted cyclopentanes.

Fraction IV (78.5-80.1°) and Fraction VI (which boiled constantly at 109.5°), according to their properties, were benzene and unchanged toluene respectively. Fraction VII was submitted to optical investigation, and it was found that, apart from a small amount of toluene, this fraction contained 50% of m-xylene, 30% of p-xylene, and about 20% of o-xylene. The residue from the fractionation of the toluene catalyzate was fractionated at 749 mm

TABLE 3

Fractional Composition of the Benzene Catalyzate

Fraction No.	Boiling range of fraction (°C)	Amount of catalyzate	n_D^{20}	d_4^{20}	Yield (% on amount of catalyzate taken for fractionation)
I	26 - 30.5	1.5	1.3545	0.6203	0.2
II	30.5 - 37.5	3.1	1.3575	0.6258	0.3
III	37.5 - 78.5	3.6	1.4820	0.8003	0.45
IV	78.5 - 80.1	33.9	1.5005	0.8788	4.2
V	80.1 -109.5	0.7	1.4965	–	–
VI	109.5	736.3	1.4960	0.8665	92
VII	109.5 -145	8.6	1.4965	0.8680	1.1
	Residue	5.4	1.5280	–	0.8

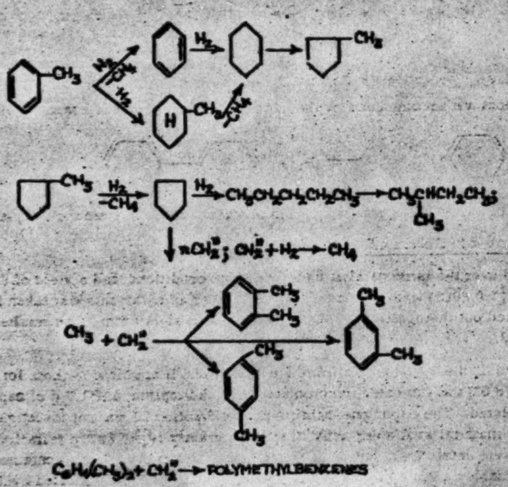
from a Favorsky flask, two fractions being obtained:

Fraction I B. p. up to 200°; 1.3 g; n_D^{20} 1.5085

Fraction II B. p. 200 - 235°; 2.1 g; n_D^{20} 1.5230

The new residue from this distillation solidified when cold to a dark-colored mass, from which it was found possible to sublime some crystals having the odor of naphthalene and melting at 71°.

Fractions I and II (up to 200°, and 200 - 235°) were treated in the cold with alcoholic picric acid. The picrates obtained (0.63 g), which formed golden-orange needles, melted at 148.5°, thus indicating that a small amount of naphthalene was present in these fractions. It would appear that the bulk of the small residue from the fractionation of the toluene catalyzate consisted of a mixture of polyalkylbenzenes, the structures of which could not be established owing to lack of material. The results of the investigation of the separate fractions of the toluene catalyzate provide the basis of the following scheme of the contact-catalysis reactions of this hydrocarbon under the given conditions:



Catalytic Treatment of Ethylbenzene

The catalytic treatment of ethylbenzene under the conditions indicated above yielded 824.5 g (97%) of liquid catalyzate having n_D^{20} 1.4975; d_4^{20} 0.8571. The analytical fractionation of 800 g of this catalyzate was carried out through a column having an efficiency of more than 100 theoretical plates at 756.8 mm. The results are given in Table 4.

TABLE 4

Fractional Composition of the Benzene Catalyzate

Fraction No.	Boiling range of fraction (°C)	Amount of catalyzate, (g)	n_D^{20}	d_4^{20}	Yield (% on amount of catalyzate taken for fractionation
I	26 - 37.5	2.2	1.3560	0.6231	0.25
II	37.5 - 77.5	5.6	1.4725	0.8007	0.7
III	77.5 - 80.5	0.8	1.4940	–	0.1
IV	80.5	116.5	1.5005	0.8769	14.5
V	80.5 - 109.5	2.2	1.4630	0.7859	0.25
VI	109.5 - 110.6	23.6	1.4960	0.8665	2.7
VII	110.6 - 133.5	0.8	1.4960	–	0.1
VIII	133.5 - 136.5	621.8	1.4965	0.8669	77.9
IX	136.5 - 148.0	4.4	1.4965	0.8670	0.5
	Residue	6.1	1.5280	0.8342	0.7

The properties of Fraction I give us reason to suppose that it was a mixture of isopentane and pentane. Benzene was removed from Fraction II by adsorption on silica gel, and the remaining part of the fraction (naphthenes and paraffins; 2.3 g) was analyzed with the aid of Raman spectra. This dearomatized fraction (d_4^{20} 0.6723; n_D^{20} 1.3920; aniline point 64.5°) was found to consist mainly of hexane isomers, including 15% of isohexane. Fraction III (77.5-80.5°) was not investigated owing to lack of material, but Fraction IV (boiling constantly at 80.5°), judging from its properties, was practically pure benzene.

Fraction V (80.5-109.5°) was subjected to chromatographic separation: it consisted of 1.1 g of an aromatic part (a mixture of benzene and toluene) and 1.0 g of a naphthene-paraffin part (n_D^{20} 1.3960 and d_4^{20} 0.7273) consisting, according to its properties, probably of heptane isomers and cycloalkanes. Fraction VI (109.5-110.6) corresponded in properties to pure toluene; Ullmann oxidation of a small part of it yielded benzoic acid, m.p. 121°. The small intermediate Fraction VII (110.6-133.5°) was not investigated. Fraction VIII (133.5-136.5°) was mainly unchanged ethylbenzene. In the oxidation products of a small part of this fraction, only benzoic acid, m.p. 120.8°, was found. Fraction IX (136.5-148°) was subjected to Ullmann oxidation, and from the mixture of acids obtained (3.9 g), 0.3 g of benzoic acid (m.p. 121°), 1.7 g of isophthalic acid, 0.73 g of terephthalic acid, and 0.8 g of phthalic acid were isolated. The isophthalic and terephthalic acids were converted into their methyl esters, which melted at 65.6° and 140° respectively.

The residue (6.1 g) from the fractionation of the catalyzate was separated by fractionation from a Favorsky flask at 758 mm into the following fractions:

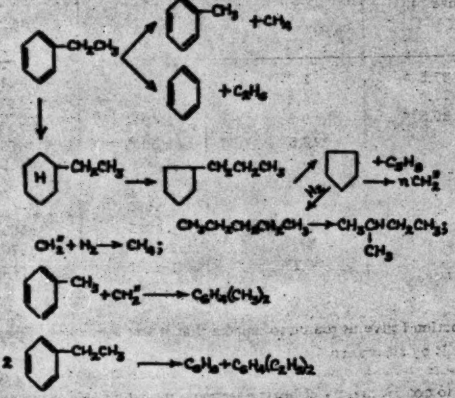
Fraction I B. p. 148 - 188°; 2.8 g; n_D^{20} 1.4960; d_4^{20} 0.8743
Fraction II B. p. 188 - 210°; 3.0 g; n_D^{20} 1.5340

The new residue consisted of a small amount of dark-colored viscous liquid, which was not investigated.

Fraction I (2.8 g) was subjected to Ullmann permanganate oxidation, and it was shown by the methods indicated above that the oxidation products included phthalic, isophthalic, and terephthalic acids. This indicates the presence in the catalyzate of isomeric diethylbenzenes formed, probably, as the result of the displacement of an ethyl group from one ethylbenzene molecule to another. In Fraction II (188-210°) the presence of naphthalene was detected; it was isolated as its picrate, m.p. 149°.

The investigation of the ethylbenzene catalyzate showed that under the given conditions the predominant reaction in the contact-catalysis transformations of ethylbenzene is partial and complete dealkylation to benzene (14.5%) and toluene (2.7%). In addition to this main reaction, the following transformations, which occur to a much less extent, also take place: transfer of an alkyl group from one ethylbenzene molecule to another, hydrogenation of the benzene nucleus and subsequent conversion of the six-membered cycle to a five-membered one, and hydrogenolysis of the latter with formation of the corresponding alkanes, which then undergo isomerization. The gas phase was analyzed in a Podbielniak apparatus: It consisted of 93 % of hydrogen, 4% of propane, and 3% of ethane and methane.

Hence, the composition of the products obtained by the treatment of ethylbenzene in an atmosphere of hydrogen in presence of a platinized alumina catalyst indicates the great variety of the reactions that occur under the given conditions. These reactions probably proceed in accordance with the following scheme:



SUMMARY

1. A study has been made of the contact-catalysis reactions of benzene, toluene, and ethylbenzene at 460° in presence of a platinized alumina catalyst and of hydrogen at a pressure of 20 atm.

2. It has been found that under the conditions used, 3.2% of the benzene, 8% of the toluene, and 22.1% of the ethylbenzene undergo far-reaching changes.

3. It has been established that the transformations of benzene proceed in the directions of hydrogenation to cyclohexane, dehydrogenation to biphenyl, and alkylation with formation of toluene and xylenes. Cyclohexane is isomerized with contraction of the ring into methylcyclopentane, which, in its turn, undergoes hydrogenolysis both in the ring and in the side chain, with formation, respectively, of hexane isomers and cyclopentane; hydrogenolysis of the cyclopentane yields pentane, part of which isomerizes into isopentane.

4. It has been found that the main reaction in the transformation of toluene and ethylbenzene is hydrogenolysis of the side chain with formation of benzene from toluene and a mixture of benzene and toluene from ethylbenzene. In both cases, however, there are simultaneous reactions of hydrogenation of the benzene nucleus, contraction of the six-membered cycle to a five-membered cycle, hydrogenolysis of the latter, and isomerization of the alkanes then formed.

5. In the catalytic treatment of the investigated aromatic hydrocarbons, there were always some products attributable to the methylation of the benzene nucleus by methylene radicals produced by decomposition of the intermediately formed cycloalkanes at the surface of the catalyst.

Received March 18, 1954.

N. D. Zelinsky Institute of Organic
Chemistry, USSR Academy of Sciences.

LITERATURE CITED

[1] B. L. Moldavsky and J. S. Bezdel, J. Gen. Chem., 16, 1633 (1946).

[2] G. L. Natanson and M. Ya. Kagan, J. Phys. Chem., 17, 381 (1943).

[3] B. Grinsfelder, H. Voge, S. Good, Ind. Eng. Chem. 37, 1168 (1945).

[4] B. G. Gavrilov and O. I. Zhgun, Sci. Mem. Leningrad State Univ., 163, 177 (1953).

[5] G. L. Thomas, J. Hoekstra, . J. T. Pinkston, J. Am. Chem. Soc. 66, 1694 (1944).

[6] Yu. G. Mamedaliev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1947, 197.

[7] R. D. Obolentsev and N. N. Gryaznov, Proc. Acad. Sci. USSR, 73, 1, 121 (1950).

[8] K. P. Lavrovsky, Yu. L. Fish, and N. N. Naimushin, Trans. Petroleum Inst., 2, 110, 1952.

[9] F. Hofmann, K. Lang, Brennstoffchemie 10, 203 (1929).

[10] K. Laider, A. Szayne, J. Inst. Petr. Technol., 20, 162 (1934).

[11] E. I. Prokonets, A. N. Filaretov, and S. M. Bogoslavskaya, J. Appl. Chem., 11, 1475 (1938).

[12] P. V. Puchkov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1937, No. 3, 482.

[13] G. N. Maslyansky, J. Gen. Chem., 14, 148 (1944).

[14] V. Haensel and Q. R. Donaldson, Ind. Eng. Chem. 43, 9, 2102 (1951).

[15] N. I. Shuikin, N. G. Berdnikova, and S. S. Novikov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, No. 2, 269.*

[16] N. I. Shuikin, N. G. Berdnikova, and S. S. Novikov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, No. 5, 879.**

[17] R. D. Obolentsev, Physical Constants of Hydrocarbons, Liquid Fuels and Oils, State Tech. Press, 1953, p. 7-8.

[18] F. Ullmann, Ber. 36, 1798 (1903).

[19] B. L. Moldavsky, G. D. Kamusher, and M. V. Kobylskaya, J. Gen. Chem., 7, 167 (1937).

---

* See Consultants Bureau Translation, p. 243.

** " " " " p. 779.

BLANK
PAGE

SYNTHESIS OF ESTERS OF POLYVINYL ALCOHOL

S. N. Ushakov and T. A. Kononova

The polymers of vinyl esters — vinyl formate, acetate, propionate, butyrate, etc. — are obtained by the polymerization of the corresponding monomers. In this case the resulting polymers are full esters, and do not contain free hydroxyl groups. In a number of cases, however, both for practical purposes and for the study of the structure and properties of the polymer, it is necessary to synthesize polymers containing definite proportions of hydroxyl groups, i.e. copolymers of vinyl alcohol and the particular vinyl ester. Such copolymers can be obtained only by controlled partial hydrolysis of a polyvinyl ester or by esterification of polyvinyl alcohol (since vinyl alcohol is unknown in the monomeric state and cannot, of course, be used as a component in copolymerization).

In other cases (for example, for the comparative study of the properties of different polymers) it is necessary to obtain polymers having the same average length of chain from esters formed by vinyl alcohol with various acids, and this again cannot be effected by the direct polymerization of the various monomers, owing to the extreme difficulty of preparing polymers that are identical both with respect to the average length of chain and with respect to the statistical distribution of the chain lengths. In this case we can approach the problem only by the careful esterification of polyvinyl alcohol of one given batch with suitable reagents that preclude the degradation of the polymer chains, or by the partial hydrolysis of polyvinyl esters. The study of processes for the esterification of polyvinyl alcohol is therefore of considerable interest. There is much information in the literature on methods of esterifying polyvinyl alcohol. Use is made of the general methods of esterification: treatment of polyvinyl alcohol with acid, anhydrides, or acid chlorides, depending on the nature of the acid residue.

The formylation of polyvinyl alcohol occurs even in absence of catalyst when the polymer is treated with formic acid at room temperature [1]. A single formylation treatment with 100% formic acid results in the formation of an ester containing 70-80 mole-% of ester groups. Complete esterification of polyvinyl alcohol is obtained by four treatments with 100% formic acid, and no chain degradation occurs. When the temperature is raised to 60° or higher, highly substituted esters are obtained immediately, but the process is accompanied by degradation of the main chain of the polyvinyl alcohol. The use of catalysts (surfuric acid, zinc chloride) leads to a reduction of the degree of substitution by formyl groups owing to partial dehydration of the polyvinyl alcohol.

The acetylation of polyvinyl alcohol has been studied by many investigators [2, 3, 4]. For acetylation it is necessary to use acetic anhydride. It may be carried out by the action of acetic anhydride on polyvinyl alcohol in pyridine [5, 6]: when polyvinyl alcohol was heated in a water bath for 24 hours with ten parts of a mixture of two parts of acetic anhydride and one part of pyridine, a polyvinyl acetate having a degree of substitution of 80 mole-% was obtained. Completely acetylated polyvinyl alcohol was obtained when polyvinyl alcohol prepared by alkaline hydrolysis was heated at 60° with a mixture of pyridine and acetic anhydride in an atmosphere of nitrogen for 20 days; the average degree of polymerization remained unchanged in this process.

Complete acetylation of polyvinyl alcohol has been effected also by the action of a mixture of acetic anhydride and acetic acid on polyvinyl alcohol pretreated by swelling in water, removal of water by suction, and dehydration with alcohol and ether [7].

Of the esters formed by polyvinyl alcohol with unsaturated monobasic acids, the methacrylic ester is known: it was prepared by the action of methacryloyl chloride on polyvinyl alcohol in absence of solvent. Also, by the action of methacrylic acid in benzene, esterification proceeded to the extent of 12-14 mole-%, and the products were insoluble in organic solvents. In this case a cross-linked polymer was formed by the participation of the double bonds of the methacrylic acid residues.

Esters of polyvinyl alcohol with dibasic acids — adipic, maleic, sebacic, and succinic — have been obtained [8] by reaction of polyvinyl alcohol with the anhydrides and acid chlorides. In the case of succinic acid only acid esters were obtained, which was confirmed by direct titration and by methylation of the carboxyls. Sebacic acid yielded full esters, and cross linking of the polyvinyl alcohol chains occurred with formation of a three-dimensional polymer.

Some polyvinyl esters, and also mixed esters, have been obtained by reaction of polyvinyl acetate with anhydrides of di- and poly-carboxylic acids in presence of water and a suitable solvent. In this way the preparation has been effected of the polyvinyl esters of succinic, glutaric, maleic, and phthalic acids, and also mixed esters of these acids [9]. When polyvinyl alcohol is esterified with citric, tartaric, maleic, and lactic acids, water-soluble derivatives are obtained, which can be used as thickening agents in the textile industry. Among the inorganic esters of polyvinyl alcohol, the nitrate and sulfate have been studied.

Several methods have been proposed for the preparation of polyvinyl nitrate [10]; they include a) treatment of a solution of polyvinyl alcohol in sulfuric acid with nitric acid; b) direct nitration with nitric acid in an atmosphere of an inert gas; c) nitration with a mixture of sulfuric and nitric acids at below 0° [11]. The sulfuric ester of polyvinyl alcohol may be obtained by treatment of polyvinyl alcohol in pyridine with chlorosulfonic acid [12].

Our investigation aimed at the development and improvement of methods for the preparation of a number of esters of polyvinyl alcohol (polyvinyl formate, acetate, propionate, butyrate, and isobutyrate) containing various proportions of free hydroxyl groups and having the same average chain length and polydispersity. As indicated above, methods for the synthesis of the formate and acetate from polyvinyl alcohol have been described in the literature, but not in relation to our present objects. There is no information in the literature about polyvinyl propionate, butyrate, and isobutyrate.

EXPERIMENTAL

The starting material was polyvinyl alcohol having an acetyl content of 1.8 mole-%. It was prepared by the alkaline alcoholysis of polyvinyl acetate in methanol and had an intrinsic viscosity of $[\eta] = 0.74$ (after reprecipitation). The whole of the work was carried out with polyvinyl alcohol that had not been reprecipitated, the fact that a partial fractionation occurs in the precipitation of our polyvinyl esters and the products of their hydrolysis being taken into account. For this reason, all comparisons of the intrinsic viscosities of polyvinyl alcohols obtained by the hydrolysis of the esters were made with the intrinsic viscosity of the reprecipitated original polyvinyl alcohol, which (in spite of some difference in the conditions of reprecipitation) gives a truer characterization of the variation of $[\eta]$ in the process of esterification and hydrolysis.

We have studied the following esters of polyvinyl alcohol: 1) the formate, 2) the acetate, 3) the propionate, 4) the butyrate, and 5) the isobutyrate. The degree of substitution by ester groups was varied from 100% to 30% (to 10% in the case of the formic ester).

For the preparation of the completely substituted formic ester, 100% formic acid was used, and for the preparation of formic esters having a low degree of substitution, aqueous formic acid at various concentrations was used. The full esters of the other acids were prepared by the action of the corresponding anhydrides on polyvinyl alcohol in pyridine at 80-95°. For the acetylation, chemically pure acetic anhydride was used, and it was vacuum-distilled before the experiment. The partially substituted esters of the homologs of formic acid were obtained by alcoholysis of the fully substituted esters. After the esterification and alcoholysis the esters were obtained as solutions, from which they were precipitated by addition to a suitable nonsolvent.

The polymers were purified by reprecipitation, and were then carefully washed and dried by the methods indicated below. The precipitation of polyvinyl formates was effected by pouring the polymer solution in a thin stream into the nonsolvent with stirring. The precipitation of the acetic, propionic, butyric, and isobutyric esters was carried out as follows. Several drops of the polymer solution were placed on the surface of water in a crystallizing dish, and they then spread over the surface and formed a thin film. The film remained for some time on the surface of the water, and the solvent diffused from it into the water. The film was then transferred to a beaker of clean water. The large surface of the precipitated polymer facilitated its thorough washing. Two precipitations of the polymer purified it completely from pyridine and acids, a result that could not be obtained by the usual method of precipitation, i.e. the pouring of the polymer solution in a thin stream into water with stirring.

Polyvinyl formates were dried in a vacuum drier at room temperature and a residual pressure of 10 mm Hg. The acetic propionic, butyric, and isobutyric acids were dried over calcium chloride at a residual pressure of 5-10 mm Hg. When the content of ester groups was not below 90-80 mole-%, the temperature of drying was about 40°; for lower contents of ester groups the esters were dried at room temperature. Polyvinyl acetates having acetyl contents of not less than 90 mole-% were given a porous structure before they were dried; this effect we obtained by the sublimation of benzene from a solution of the polymer [13].

Polyvinyl acetates having acetyl contents of 70-45 mole-% were insoluble in benzene and formed a compact mass when vacuum-dried. It was practically impossible to remove water from this mass, and the esters were therefore dried by means of high-frequency currents, a 1-kw laboratory apparatus working at a wavelength of 5 μ and a frequency of $5.4 \cdot 10^7$ cycles per second being used.

The content of ester groups in the polyvinyl esters was determined by hydrolysis of a weighed amount of ester (0.2-0.4 g) with alkali at the boil for eight hours, the excess of alkali being titrated to phenolphthalein with 0.1 N HCl. The alkali used was 0.1 N aqueous NaOH in the case of polyvinyl formate, and 0.1 N alcoholic KOH in the case of polyvinyl acetate, propionate, butyrate, and isobutyrate.

Polyvinyl Formates. The fully substituted formic ester of polyvinyl alcohol was prepared by a previously described method [1]. A weighed amount of polyvinyl alcohol was covered with six times the weight of 100% formic acid and set aside at room temperature (16-18°) for 50 hours. In the course of this time the whole of the polyvinyl alcohol passed into solution. The solution was then diluted with acetone so as to bring the concentration of ester in the solution to 5-6%, and the polymer was precipitated by pouring the solution gradually into ethanol. It was then carefully washed with alcohol until neutral, and vacuum-dried (10-12 mm Hg) at room temperature. In order to attain 100% substitution, the formylation was performed four times successively (Table 1).

TABLE 1

Content of Formate Groups in the Ester after Successive Formylations

	Content of formate groups		Solvent
	% by weight	mole-%	
Formylation I	57	86.0	Acetone, pyridine
Formylation II	60	93.6	Dioxane, chloroform
Formylation III	61.2	96.6	Dioxane, chloroform
Formylation IV	62.2	99.2	Dioxane, chloroform

Formic esters having contents of ester groups of less than 80 mole-% have not been described in the literature. We have prepared such esters by the formylation of polyvinyl alcohol both by 100% formic acid and also by diluted acid, the temperature of the reaction and its duration being varied according to the degree of esterification required. The results of the experiments are given in Table 2. Polyvinyl formates having a degree of substitution of more than 70 mole-% were precipitated from acetone by means of methanol or ethanol (the polyvinyl formate having a degree of substitution of 10% was precipitated from the reaction mixture by means of methanol), when they formed threads, which were converted into white opaque pieces when vaccum-dried for 50-70 hours. For degrees of substitution of 68-36 mole-%, the reaction mixture was precipitated in alcohol as a slimy material, which was carefully and repeatedly washed with alcohol until neutral, and then finally washed with ether. The polymer was then placed on glass in the form of a thin layer and was vacuum-dried at room temperature. In spite of the fact that the films acquired a porous structure owing to the rapid evaporation of the ether, drying to constant weight lasted for 150-200 hours.

The fully substituted polyvinyl formate obtained from polyvinyl alcohol was hydrolyzed to polyvinyl alcohol by treatment at the boil for six hours with 5% aqueous formic acid. For the polyvinyl alcohol so obtained the intrinsic viscosity was determined graphically ($[\eta] = 0.77$).

TABLE 2

Dependence of the Content of Formate Groups in Esterified Polyvinyl Alcohol on the Concentration of the Esterifying Formic Acid, on the Temperature, and on the Duration of the Reaction

Concentration of formic acid (%)	Bath ratio	Reaction temperature (°C)	Duration of reaction (hours)	Content of formate groups		Solvent used for the production of the film
				% by weight	mole-%	
100	1:6	18	24	53.3	78.0	Acetone
78	1:10	18	30	49.6	68.7	80 % aqueous acetone
100	1:6	18	4	41.0	53.8	75 % aqueous acetone
78	1:10	0	15	37.7	48.1	85 % aqueous acetone
78	1:10	-2	6	30.0	36.3	50 % aqueous acetone
35•	1:20	18	2	10.0	10.4	

Polyvinyl Acetate. The acetic ester of polyvinyl alcohol was prepared by the esterification of polyvinyl alcohol with acetic anhydride in a pyridine medium. The reaction was carried out as follows: polyvinyl alcohol (4 g) was covered with pyridine (35 ml), and the mixture was set aside at room temperature for twelve hours. Acetic

---

• In this case the polyvinyl alcohol was first dissolved in water, and then formic acid was added to the 70% aqueous solution in such amount that its concentration in the solution was 35%.

anhydride (30 ml) was then added, and the mixture was heated in a boiling water bath. After 30 minutes the polymer has swollen so much that the stirrer could no longer operate in the reaction mixture. After one hour the whole of the polymer had gone into solution. After three hours from the beginning of the reaction the mixture was cooled and diluted with 50 ml of acetone; the mixture was quite colorless. The polymer was precipitated from solution in a large amount of water; it was carefully washed free from reaction products and then dried. It was then again precipitated from an acetone solution into water. Before being dried for analysis the polymer was given a porous structure by the sublimation of benzene from a solution of the polymer. The content of ester groups in the ester so obtained was 98.5 mole-%. In order to check for the absence of chain degradation in the course of the reaction, the polyvinyl acetate was saponified to polyvinyl alcohol by alcoholysis in absolute methanol containing 0.4% of KOH. The intrinsic viscosity of the polyvinyl alcohol so obtained was determined ($[\eta] = 0.72$).

In order to obtain partially substituted polyvinyl acetates, the polyvinyl acetate from which the polyvinyl alcohol used in this work was prepared was subjected to saponification, which was carried out in absolute methanol at a bath ratio of 1:6 with various amounts of KOH for 13-15 hours at room temperature. After 13-15 hours the reaction mixture was diluted with acetone (Expt. No. 1 and 2, Table 3) or aqueous acetone (Expt. No. 3 and 4), and the polymer was precipitated in water. The polymers from Expt. No. 2, 3, and 4 precipitated in the form of slimy material, and when they were air-dried a crust formed on their surfaces which prevented further drying. These polymers, therefore, were first dried with the aid of high-frequency currents and then under a reduced pressure of 10 mm Hg at 20-25°. The vacuum drying was continued for 50-70 hours.

Polyvinyl Propionate. As indicated above, propionic esters of polyvinyl alcohol have not been described in the literature. We have prepared the fully substituted propionic ester of polyvinyl alcohol by the esterification of polyvinyl alcohol with propionic anhydride in pyridine. The reaction was carried out as follows: polyvinyl alcohol (4 g) was covered with pyridine (30 ml), and the mixture was set aside at room temperature for twelve hours. The mixture was then stirred, and propionic anhydride (15 ml, i.e. 1.25 mole per mole of polyvinyl alcohol) was added. The mixture was heated in a boiling water bath, and after one hour the polyvinyl alcohol had swollen to such and extent that the stirrer could no longer operate in the reaction mixture. After 90 minutes the mixture had become thinner, and after three hours the whole of the polymer had passed into solution. After five hours from the beginning of the reaction, heating was discontinued, the solution was cooled, and 60 ml of acetone was added. The solution was yellow. The polymer was precipitated from solution in a large amount of water; it was then carefully washed with water and dried for 30 hours at 10 mm Hg and at 45°. It was then reprecipitated, carefully washed, and dried under the same conditions to constant weight (50 hours). The content of ester groups was 72.5% by weight, or 98.5 mole-%.

TABLE 3

Saponification Conditions, and the Properties of Polyvinyl Acetates

Expt. No.	Amount of KOH (%)	Duration (hours)	Form of reaction mixture	Diluent	Content of acetate groups in polymer	
					% by weight	mole-%
1	0.05	14	Liquid	Acetone	58.0	70.8
2	0.15	14	Liquid	Acetone	54.3	66.0
3	0.25	15	Gel	60% Aqueous acetone	50.4	58.5
4	0.32	15	Gel	50% Aqueous acetone	43.4	45.5

Propionic esters of polyvinyl alcohol having various contents of ester groups were obtained by saponification of the 98.5% ester in absolute methanol by means of various amounts of KOH at room temperature (Table 4). The reaction mixture was poured into water, and the product was carefully washed with water for 48 hours and dried at room temperature at a residual pressure of 10 mm Hg. The saponification of the polyvinyl propionate obtained to polyvinyl alcohol was carried out with 1% KOH in absolute methanol. The intrinsic viscosity of the polyvinyl alcohol obtained was $[\eta] = 0.77$.

Polyvinyl Butyrate. Butyric esters of polyvinyl alcohol have not been described in the literature. We have prepared the fully substituted butyric ester of polyvinyl alcohol by the esterification of polyvinyl alcohol with butyric anhydride in pyridine. The reaction was carried out in a similar way to that for polyvinyl propionate. Before precipitation of the polymer, the reaction mixture was diluted with methanol. The polymer was precipitated in water, but the films stuck together when washed with water in the beaker. After being washed for 48 hours, the polymer was dried in a vacuum drier at 40° and 10 mm Hg for ten hours. It was then dissolved in ethanol and precipitated in water; this time the films did not stick together during washing. Drying to constant weight was carried out in a vacuum drier at 40° and 10 mm Hg. The product was a compact piece of light-brown rubberlike polymer having an ester-group content of 99.95 mole-%.

TABLE 4

Saponification Conditions, and the Properties of Polyvinyl Propionates

Expt. No.	Amount of KOH (%)	Duration (hours)	Form of reaction mixture	Diluent	Content of ester groups	
					% by weight	mole-%
1	0.2	13	Liquid	Acetone	62.5	72.6
2	0.3	16	"	"	52.8	53.4
3	0.4	14	Gel	50% Aqueous acetone	40.0	34.7
4	1.0	24	"	Water	2.0	1.2

Butyric esters of polyvinyl alcohol containing various proportions of ester groups were obtained by the saponification of the 100% ester in absolute methanol at room temperature with various amounts of KOH (Table 5, Expt. No. 1,2, and 3).

The esters obtained were precipitated in water, carefully washed with water for 48 hours, and dried at room temperature at a residual pressure of 10 mm Hg. The intrinsic viscosity of the polyvinyl alcohol obtained from polyvinyl buyrate by saponification was [η] = 0.78.

TABLE 5

Saponification Conditions, and the Properties of Polyvinyl Butyrates

Expt. No.	Amount of KOH (%)	Duration (hours)	Form of reaction mixture	Diluent	Content of ester groups	
					% by weight	mole-%
1	0.5	14	Liquid	Acetone	68.3	76.4
2	0.6	14	"	Methanol	64.2	67.0
3	1.0	12	Gel	50% Aqueous ethanol	43.5	35.4
4	2.0	15	"	Water	2.0	1.0

Polyvinyl Isobutyrate. Isobutyric esters of polyvinyl alcohol have not been described in the literature. We have prepared an almost fully substituted isobutyric ester of polyvinyl alcohol by the esterification of polyvinyl alcohol with isobutyric anhydride in pyridine. The course of the reaction was similar to that of butyric anhydride; it was complete in nine hours. The content of ester groups in the product was 75.3% by weight, or 96.7 mole-%. Isobutyric esters of polyvinyl alcohol having different proportions of ester groups were prepared by the saponification of the 96.7% ester in absolute methanol at room temperature with various amounts of KOH (Table 6, Expt. No. 1, 2, and 3).

TABLE 6

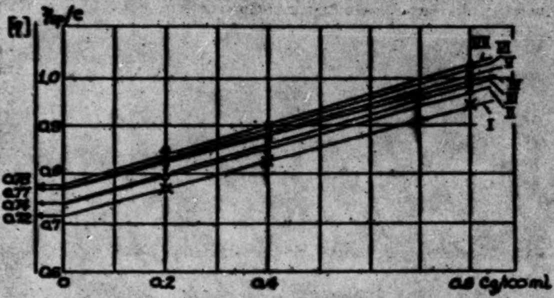
Saponification Conditions, and the Properties of Polyvinyl Isobutyrate

Expt. No.	Amount of KOH (%)	Duration (hours)	Form of reaction mixture	Diluent	Content of ester groups	
					% by weight	mole-%
1	0.75	14	Liquid	Ethanol	68.5	77.70
2	1.0	18	Viscous liquid	50% Aqueous ethanol	58.5	56.0
3	2.0	20	Gel	80% Aqueous methanol	44.3	34.7
4	4.0	48	"	Water	2.4	1.4

The esters obtained were precipitated in water, carefully washed with water for 48 hours, and dried at room temperature at a residual pressure of 10 mm Hg.

Polyvinyl alcohol obtained from polyvinyl isobutyrate had an intrinsic viscosity of [η] = 0.73.

The dependence of η_{sp}/C on $\underline{C}$ for polyvinyl alcohols obtained from various esters is shown graphically in the figure.



Dependence of η_{sp}/C on C for polyvinyl alcohols obtained from various esters: 1 - from polyvinyl acetate; 2 - from polyvinyl isobutyrate; 3 – the original reprecipitated sample; 4 - from polyvinyl formate; 5 - from polyvinyl propionate; 6 - from polyvinyl formate; 7 - from polyvinyl butyrate

SUMMARY

1. The syntheses have been effected of esters of polyvinyl alcohol with the following acids: formic, acetic, propionic, butyric, and isobutyric (the last three have not been described previously). The degree of substitution varied from 100 to 30 mole-% (to 10 mole-% in the case of polyvinyl formate).

2. The preparation of these polyvinyl esters was accompanied by the maintenance of the mean length of the macromolecular chains within comparable limits. This was shown by saponifying the esters to polyvinyl alcohol and comparing the intrinsic viscosities of the products with that of the polyvinyl alcohol from which the esters were prepared. The intrinsic viscosities of the polyvinyl alcohols obtained from the various polymers varied within the limits [η] = 0.72-0.78, while the intrinsic viscosity of the original (reprecipitated) polyvinyl alcohol was 0.74.

3. Various methods were used for the preparation of these esters of polyvinyl alcohol. Formic esters of polyvinyl alcohol having various degrees of substitution were synthesized by treatment of the polyvinyl alcohol with formic acid of various concentrations. For the preparation of almost fully substituted acetic, propionic, butyric, and isobutyric esters, the general method of esterification was used in which the polyvinyl alcohol is treated with the anhydride of the corresponding acid in a pyridine medium. Partial esters were obtained by partial alcoholysis of the full esters in methanol containing KOH at various concentrations.

Received April 23, 1954

Lensoviet Leningrad Institute of Technology

LITERATURE CITED

[1] S. N. Ushakov, R. K. Gavurina, and B. P. Chekhovskaya, Bull. Acad. Sci. USSR, Div.Chem.Sci.1947,No.1,71.
[2] H. Staudinger, Gray, Stark, Ber. 60, 1782 (1927).
[3] H. Staudinger, Ber. 59, 3019 (1926).
[4] H. Staudinger, Ber. 60, 1658 (1927).
[5] Marvel, Inskeep, J. Am. Chem. Soc. 65, 1710 (1943).
[6] H. Staudinger, J. prakt. Chem. 155, 261 (1946).
[7] V. V. Korshak and V. A. Zamyatina, Bull. Acad. Sci. USSR, Div.Chem. Sci., 1946, No.1, 106.
[8] S. N. Ushakov, R. K. Gavurina, and P. A. Medvedeva, J. Appl. Chem., 21, No. 11 (1948).
[9] J. Jones, British Plastics 15, 380 (1943).
[10] S. N. Ushakov, Collection of Papers on Synthetic Resins and Plastics, No. 4, 63-76, 1945, State Chem. Press.
[11] British Pat. No. 924114.
[12] F. Kainer, Polyvinylalkohol, 1949.
[13] F. Levis, Fr. Muge, Ind. Eng. Chem., An. Ed. 27, 3, 134 (1945).

REACTIONS OF UNSATURATED AND MACROMOLECULAR COMPOUNDS

COMMUNICATION 4. COPOLYMERIZATION OF SOME VINYL COMPOUNDS WITH 2-VINYLOXYETHANOL

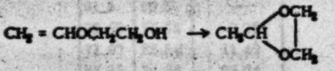
M. F. Shostakovsky and A. M. Khomutov

Investigations of polymerization and copolymerization reactions of vinyl ethers and acrylic acid derivatives have shown that the formation of polymers and copolymers by a free-radical mechanism is in principle possible [1, 2, 3]. In the course of these studies the laws governing these reactions, and also the nature of the initiator, have been revealed. An important factor in the effecting of this reaction is the choice of initiator [4]. An essential condition with respect to the nature of the radical is that its free valency must not belong to oxygen. These considerations apply mainly to the initiation of the reaction of vinyl ethers by the free-radical mechanism, and they are probably of great importance in other cases also. The course of polymerization and copolymerization depends on the reactivities of the monomers, which are determined not only by the double bonds, but also by the presence, for example, of the mobile hydrogen of hydroxyl groups, etc.

A defect of earlier investigations has been that the decomposition of, for example, benzoyl peroxide has been treated in an extremely schematic manner and only the reaction of double bonds has been taken into consideration. The investigations in this field, however, show that these reactions have many aspects and are accompanied by a number of side reactions, which have been established by us by a study of the reaction products, and which confirm the complicated mutual effects of atoms in the molecule that were predicted by the great Russian chemist Markovnikov [5].

In the present investigations we have examined the copolymerization of 2-vinyloxyethanol with methacrylic acid, with methyl methacrylate, and with styrene.

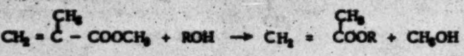
2-Vinyloxyethanol [6] $OHCH_2CH_2OCH=CH_2$ contains clearly defined reaction centers: the double bond, the oxonium oxygen, and the hydroxyl with the mobile hydrogen. Such a structure confers a number of peculiar properties on the substance. Thus, 2-vinyloxyethanol readily isomerizes, and under the usual conditions exists in the associated state [7]:



Accordingly, 2-vinyloxyethanol does not polymerize under the influence of metal chlorides and acids [8].

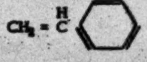
On the basis of these properties of 2-vinyloxyethanol, it would be expected that, in reacting with methacrylic acid or methyl methacrylate, copolymerization would occur with participation of the double bonds, and that reactions would occur in which the functional groups would take part.

As indicated above, as copolymerization components we used methacrylic acid, methyl methacrylate, and styrene. These vinyl compounds have a number of chemical peculiarities. Thus, methacrylic acid gives "acylals" with vinyl ethers; methyl methacrylate is capable of undergoing alcoholysis [9]:



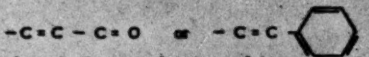
$$CH_2=\overset{CH_3}{C}-COOCH_3 + ROH \rightarrow CH_2=\overset{CH_3}{C}OOR + CH_3OH$$

Styrene has a very reactive double bond [9]; its phenyl group is not reactive. Styrene has a structure in which a double bond is conjugated with a benzene nucleus:

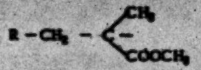


Our investigations show that 2-vinyloxyethanol copolymerizes with methacrylic acid and with methyl methacrylate, but not with styrene.

From this we may assume that, when the free radical of the initiator reacts with a molecule containing a conjugated bond system

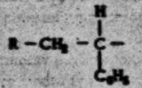


a complex radical is formed. However, the nature of this conjugation has a marked effect on the nature of the more complex radical formed, and the radicals vary in behavior: thus the radical



$$R-CH_2-C(CH_3)(COOCH_3)-$$

is more active than the radical



$$R-CH_2-C(H)(C_6H_5)-$$

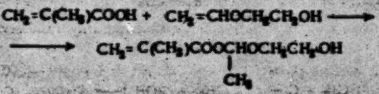
Our study of the interaction of methacrylic acid and 2-vinyloxyethanol has shown that the formation of copolymers occurs. Increase in the amount of 2-vinyloxyethanol in the reaction medium results in a reduction in yield of copolymer and an increase in the proportion of vinyloxyethanol residues in the chain (Table 1). Similar behavior has been observed for other vinyl ethers [1].

In the analysis of the copolymers, not only carboxyl groups, but also acetaldehyde was found, thus indicating the presence of "acylals", which could be formed during the reaction as indicated in the following schemes:

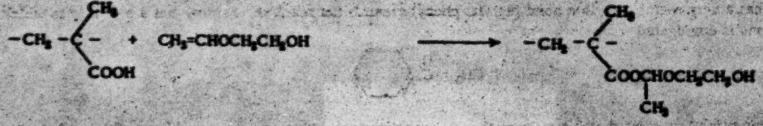
TABLE 1

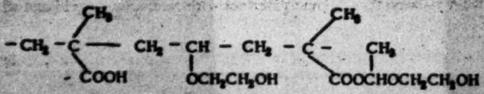
Yields and Compositions of Copolymers of Methacrylic Acid and 2-Vinyloxyethanol

No.	Molar ratio (%)		Yield (%)	Analysis of copolymer		Composition of copolymer (%)	
	$CH_2=C(CH_3)COOH$	$CH_2=CHOCH_2CH_2OH$		methacrylic acid (%)	2-vinyloxyethanol (%)	$-CH_2-C(CH_3)(COOH)-$	$CH_3-C(H)(OCH_2CH_2OH)-$
1	100	–	91.5	99.5	–	100	–
2	95	5	78.63	96.75	3.25	96.82	3.18
3	75	25	71.07	88.58	11.42	88.82	11.18
4	50	50	57.35	74.66	25.34	75.05	24.95
5	25	75	41.24	66.2	34.8	66.85	33.15
6	5	95	13.14	40.85	59.15	41.64	58.36
7	–	100	Nil	–	–	–	–

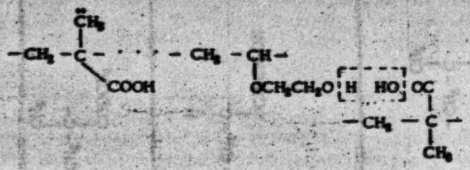


$$CH_2=C(CH_3)COOH + CH_2=CHOCH_2CH_2OH \longrightarrow CH_2=C(CH_3)COOCH(CH_3)OCH_2CH_2OH$$

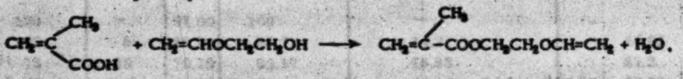




Unlike previously described [3] copolymers of methacrylic acid and vinyl ethers, those obtained from the pairs of monomers used in this investigation are insoluble substances that swell in the usual solvents. It may be pointed out here that cross-linking of the macromolecules is observed for equimolecular proportions of monomers, or when there is an excess of 2-vinyloxyethanol. Since vinyl ethers that do not contain a hydroxyl group do not give cross-linking, the occurrence of the phenomenon in the present case must be attributed to the hydroxyl of 2-vinyloxyethanol.

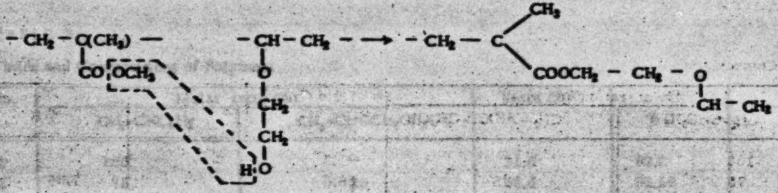


or first of all a divinyl compound is formed:

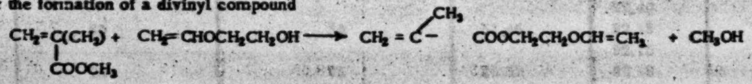

$CH_2=C(CH_3)COOH + CH_2=CHOCH_2CH_2OH \longrightarrow CH_2=C(CH_3)-COOCH_2CH_2OCH=CH_2 + H_2O.$

which then takes part in the copolymerization reaction.

We will pass to a discussion of the copolymerization of the other member of the acrylic series, methyl methacrylate, with 2-vinyloxyethanol. In this case also, with increase in the concentration of 2-vinyloxyethanol the yield of copolymer falls and the proportion of 2-vinyloxyethanol residues in the chain rises. When the proportion of 2-vinyloxyethanol in the reaction mixture exceeds 50 mole-%, the formation of a three-dimensional polymer is observed, which is probably to be attributed to alcoholysis:



or the formation of a divinyl compound


$CH_2=C(CH_3)COOCH_3 + CH_2=CHOCH_2CH_2OH \longrightarrow CH_2=C(CH_3)-COOCH_2CH_2OCH=CH_2 + CH_3OH$

which then takes part in the copolymerization reaction. In the same medium, simultaneously with the three-dimensional polymers, copolymers of good solubility in acetone are formed. These, however, do not correspond in composition to a polymer of methyl methacrylate (Table 2). Since these two monomers have almost the same carbon contents, the compositions of the copolymers were determined by analysis for functional groups (Table 2).

Experiments on the copolymerization of styrene and 2-vinyloxyethanol did not yield positive results: in all cases polystyrene was isolated (Table 3).

EXPERIMENTAL

The monomers used in this investigation were freshly distilled, and their constants were as follows. Methacrylic acid: b.p. 160°; n_D^{20} 1.4313; d_4^{20} 1.0153; acid number 650 ml of KOH. Methyl methacrylate: b. p. 100.5°; n_D^{20} 1.4150; d_4^{20} 0.936. Styrene: b.p. 146°; n_D^{20} 1.5420; d_4^{20} 0.9072.

2-Vinyloxyethanol: b.p. 140°; n_D^{20} 1.4368; d_4^{20} 0.9805; Methanol: b. p. 64-65°; n_D^{20} 1.3300; Benzene: b. p. 80-80.5°; n_D^{20} 1.5010; Acetone: b. p. 56°; n_D^{20} 1.3595.

TABLE 2

Yields and Compositions of Copolymers of Methyl Methacrylate and 2-Vinyloxyethanol

No.	Molar ratio (%)		Yield	Ratio of monomer units in copolymer by analysis (%)		Composition of copolymer (mole-%)	
	$CH_2=C(CH_3)COOCH_3$	$CH_2=CHOCH_2CH_2OH$		$-CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-$	$-CH_2-\underset{OCH_2CH_2OH}{\overset{H}{C}}-$	$-CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-$	$CH_2-\underset{OCH_2CH_2OH}{\overset{H}{C}}-$
1	100	–	97.00	100	–		
2	95	5	88.2	85.7	14.3	84.06	15.94
3	75	25	70.12	83.17	16.83	81.3	18.7
4	55	50	62.00	56.0	44.0*	50.66	79.34
5	25	75	29.00	51.39	48.61	48.20	51.8
6	5	95	10.23	33.9	66.1	31.10	68.90
7	—	100	Nil	–	–	–	–

* Composition of the copolymer as calculated from elementary analysis for C and H: methyl methacrylate residues 56.9%, 2-vinyloxyethanol units 43.1 mole %.

TABLE 3

Yields and Compositions of Polymers

No.	Molar ratio (%)		Yield (%)	%C	%H
	$CH_2=CHC_6H_5$	$CH_2=CHOCH_2CH_2OH$			
1	100	–	91.0	92.2	
2	75	25	58.6	92.52	7.66
				92.40	7.85
3	50	50	51.46	92.15	7.73
				92.15	7.87
4	25	75	18.59	92.19	8.07
				91.95	7.99

Experimental Procedure

The copolymerization was carried out in sealed glass tubes at 60 ± 1°. The total amount of the starting materials, which were taken in various proportions, was 10 g. and 0.2% of benzoyl peroxide on the total weight of monomers was added. The process proceeded continuously for 100 hours, when solid or highly viscous products were obtained. Control experiments on the polymerization of the separate monomers were carried out in presence of benzoyl peroxide under the same conditions. When the process was complete, the tubes were cooled to 0°. The reaction products were purified by bringing them into solution and then reprecipitating them. In those cases in which no reaction could be established by the formation of precipitates, the contents of the tube were fractionally distilled.

When polymers were present, dissolution and reprecipitation were repeated until removal of the original monomers was complete. The macromolecular products were then dried to constant weight. The compositions of the copolymers were then determined. The solutions obtained after precipitation and dissolution were vacuum-factionated in a system having cooled traps. The residue in the distillation flask was dried to constant weight. The amounts of the original monomers in the distillates were determined. On the basis of the results so obtained the compositions of the copolymers were calculated and the general balance sheet of the reaction products was made out. We give here the most characteristic results from numerous investigations of copolymerization.

1. Copolymerization of methacrylic acid and 2-vinyloxyethanol

The amounts taken for the copolymerization were 5 g of methacrylic acid and 5 g of 2-vinyloxyethanol (molar ratio 1:1). The conditions of the copolymerization and the method of isolating the copolymers are described above. The resulting copolymer was a swollen gel, insoluble in methanol; it was treated with ether until there were no longer reactions for double bonds and carboxyl groups. Since the carbon contents of the original monomers were not greatly different – 55.8% for methacrylic acid and 54.54% for 2-vinyloxyethanol – the determination of the elementary composition served no purpose in this case. The compositions of the copolymers were therefore established by carboxyl estimations (in the control sample of methacrylic acid polymer, 99-100% of the carboxyl content was accounted for by titration).

The materials isolated as a result of these investigations were: a) 5.7346 g of copolymer; b) 3.8178 g of material remaining in the distillation flask after the fractionation; c) 0.1 g of methacrylic acid and 0.12 g of 2-vinyloxyethanol, which were determined by titration of a mixture of solvent and precipitant. The total amount accounted for was 9.74 g, which is 97.4% of the weight of the monomers taken for reaction.

Analysis of the copolymer showed that it contained 57.8% of carboxyl groups, which corresponds to the same percentage content of methacrylic acid. The residue in the distillation flask was also analyzed for carboxyl content, and acetaldehyde was determined titrimetrically (by the iodometric method). It was found that carboxyl groups and acetaldehyde were present.

The copolymerization of these monomers was studied also for other molar ratios. When reaction was complete, the products were treated under the conditions of the above-described experiment. The results of the investigation of these copolymers are given in Table 1.

Thus, the copolymers contained methacrylic acid and 2-vinyloxyethanol units and acylal groupings.

2. Copolymerization of $CH_2=C(CH_3)COOCH_3$ and $CH_2=CHOCH_2CH_2OH$ (molar ratio 1:1)

The amounts taken for the copolymerization were 2.65 g of methyl methacrylate and 2.35 g of 2-vinyloxyethanol. The conditions of the copolymerization and the method of purifying the copolymers are described above. The copolymer was not completely soluble in acetone; the solution contained a swollen gel, which was treated with acetone and then ether until there was no longer a reaction for double bonds. The copolymer gel was dried, and the yield was found to be 2.67 g. The solution (0.5 ml) obtained after the separation and purification of the copolymer gave no precipitate with methanol. It gave a precipitate with water, however, and the whole of the solution was therefore slowly poured into water. The resulting precipitate was washed until there was no longer a reaction for a double bond, and was then dried and weighed (0.43 g).

Two products were therefore isolated. Elementary analysis showed that they contained 57.78% C (gel) and 58.30% C (soluble copolymer). As the carbon contents of the original monomers differed by only 5.5%, the compositions of the copolymers were established by estimation of the 2-vinyloxyethanol hydroxyl groups. Methyl methacrylate was determined by titration in the solutions remaining after separation of the copolymers.

After distillation of this solution, followed by drying under reduced pressure, 1.63 g of liquid remained in the distillation flask; this was found to be a mixture of the original monomers and products of their reaction. Hence, from the original 5 g of monomers, 4.83 g of products were isolated.

The copolymerization of these monomers was studied also for other molar ratios. When reaction was complete, the products were treated under the conditions of the previous experiments. The results of the investigation of these copolymers are given in Table 2.

It may be pointed out that, when the reaction was carried out at a molar ratio of 1:3 ($CH_2=C(CH_3)COOCH_3$ and $CH_2=CHOCH_2CH_2OH$), the resulting copolymers were insoluble in acetone, but when the inverse ratio was used (3:1) the copolymers dissolved readily in acetone.

3. Interaction of $CH_2=CHC_6H_5$ and $CH_2=CHOCH_2CH_2OH$

These monomers were investigated at various molar ratios. The polymerization conditions are described above. The resulting polymers were treated with methanol until there was no longer a reaction for double bonds. They were then dried and analyzed for C and H contents. Results for several ratios are given in Table 3, from which it will be seen that in all of these experiments pure polystyrene was isolated, i.e. no copolymerization occurred.

SUMMARY

1. Copolymers of 2-vinyloxyethanol with methacrylic acid and with methyl methacrylate have been prepared.

2. It has been shown that increase in the proportion of 2-vinyloxyethanol in the reaction mixture results in lower yields of copolymers and in the formation of three-dimensional copolymers.

3. It has been shown that styrene does not form copolymers with 2-vinyloxyethanol in presence of benzoyl peroxide.

Received September 25, 1953

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

LITERATURE CITED

[1] M. F. Shostakovsky and A. M. Khomutov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, No. 6, 1049. *

[2] M. F. Shostakovsky, I. A. Chekulaeva, and A. M. Khomutov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 2, 323. **

[3] M. F. Shostakovsky and A. M. Khomutov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 3, 484.***

[4] M. F. Shostakovsky and A. M. Khomutov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 5, 924.

[5] V. V. Markovnikov, Material relating to the Mutual Effects of Atoms in Chemical Compounds. Univ. Press, Kazan, 1869.

[6] M. F. Shostakovsky and G. P. Gracheva, J. Gen. Chem., 19, 1250 (1949).****

[7] M. F. Shostakovsky, M. I. Batuev, and P. V. Tyupaev, Proc. Acad. Sci. USSR, 89, 801 (1953).

[8] M. F. Shostakovsky, Vinyl Ethers, Acad. Sci. USSR Press, 1952, p. 98.

[9] Monomers (Collection of Papers), 1951, p. 141, 177.

---

* See Consultants Bureau Translation, p. 931.

** " " " " p. 263.

*** " " " " p. 411.

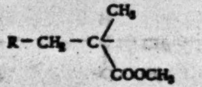
**** " " " " p. 1243.

REACTIONS OF UNSATURATED AND MACROMOLECULAR COMPOUNDS

COMMUNICATION 5. COPOLYMERIZATION OF METHYL ACRYLATE WITH VINYL ETHERS

M. F. Shostakovsky and A. M. Khomutov

Investigations of the polymerization and copolymerization reactions of methacrylic acid, methyl methacrylate, and various vinyl ethers have resulted in a considerable extension of our ideas in this field [1, 2, 3]. For example, these investigations have established the importance of the nature of the radicals present, particularly those formed by the decomposition of benzoyl peroxide. These radicals are unable to initiate the polymerization of vinyl ethers, and we consider that their ineffectiveness is to be explained by the fact that in these radicals the free valency is on oxygen. Radicals having free valencies on C, N, S, and other elements have initiating properties also for the reactions of vinyl ethers. As regards the part played by benzoyl peroxide and the radicals formed by its decomposition in copolymerization reactions with derivatives of methacrylic acid, the initiating radicals attack the methacrylic acid derivative so that a complex radical of the following structure is formed:

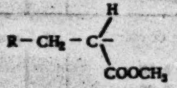


$$R-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}$$

This has its free valency on carbon and can now draw vinyl ethers into a copolymerization reaction. It has been pointed out that the presence of conjugated double bonds in the complex radical referred to above has a favorable influence on the initiation of the copolymerization of vinyl ethers [4, 5].

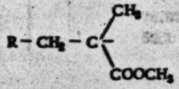
Apart from these factors, the concentration of the vinyl ether affects the course of the copolymerization process, and as this concentration increases, the proportion of vinyl ether units in the copolymer chain also increases. The extension of our ideas on polymerization and copolymerization has resulted from the direction of our studies to the reactions of compounds similar in general structure, but differing from one another by the presence of different substituents. The enables us to obtain a clear picture of the effects of atoms and groups in the molecules, as expounded in the teaching of Markovnikov [6].

In spite of the fact that methacrylic acid derivatives differ from the corresponding derivatives of acrylic acid only in the presence of the 2-methyl group, there are considerable differences in the courses of the corresponding polymerization and copolymerization reactions and in the properties of the products of these reactions. This gives reason to suppose that the initiating effect of the complex radical



$$R-CH_2-\overset{H}{\underset{COOCH_3}{C}}-$$

is probably greater than for the corresponding radical from methyl methacrylate



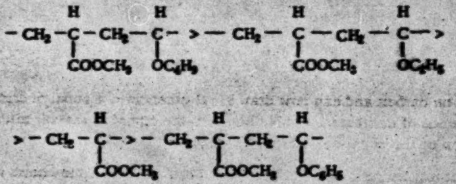
$$R-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}-$$

The copolymerization reaction and the properties of the radical have now been studied for methyl acrylate and vinyl ethers as reactants, and it has been found that in this reaction methyl acrylate is more reactive than methyl methacrylate. The polyacrylate differs from the polymethacrylate in that its ester groups can be readily and quantitatively removed by hydrolysis.

Finally, it must be pointed out that the polymers and copolymers obtained are more elastic than the corresponding products obtained from methyl methacrylate. There are only isolated references in the literature to the copolymerization of methyl acrylate with vinyl ethers [7]. There are references to examples of emulsion copolymerization and to the marketing of a number of commercial products. There are no data relating to the course of these reactions, however: there is only the statement that radicals derived from alkyl vinyl ethers are about the same in activity as that derived from vinyl acetate with respect to their behavior towards methyl acrylate monomer [8]; it is also concluded that alkyl vinyl ethers do not yield macromolecular compounds with, for example, vinyl acetate. Apart from these, there are no data in the literature on the copolymerization of vinyl ethers with methyl acrylate. The copolymerization reactions of vinyl ethers with acrylic acid derivatives are nevertheless of great interest. We have therefore investigated the reactivities of vinyl ethers and methyl acrylate in such reactions. A study of the course of the reactions and the compositions of the copolymers has shown that with increase in the concentration of vinyl ethers in the reaction medium the yields of copolymer fall and the proportion of vinyl ether units in the copolymer chain rises. A comparison of the compositions, structures, and properties of the copolymers of vinyl ethers with methyl methacrylate and with methyl acrylate reveals considerable differences, including the difference in the proportion of ester units in the chain, the proportion of methacrylate residues being the greater (Table 1).

Table 1 gives the compositions of the copolymers, as derived from elementary analysis and the results of the hydrolysis of the ester groups of the methyl acrylate units.

With regard to the properties of the copolymers, it may be noted that copolymers formed by methyl acrylate with alkyl vinyl ethers are more highly elastic than polymethyl acrylate. If, however, the copolymer contains phenyl vinyl ether units, the elasticity is considerably reduced. With respect to elasticity, methyl acrylate polymers and copolymers can be placed in the following series (the formulas are conventionalized):

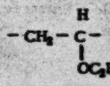
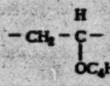
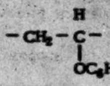


$$-CH_2-\underset{COOCH_3}{\overset{H}{C}}-CH_2-\underset{OC_4H_9}{\overset{H}{C}}- > -CH_2-\underset{COOCH_3}{\overset{H}{C}}-CH_2-\underset{OC_6H_5}{\overset{H}{C}}- >$$

$$> -CH_2-\underset{COOCH_3}{\overset{H}{C}}- > -CH_2-\underset{COOCH_3}{\overset{H}{C}}-CH_2-\underset{OC_6H_5}{\overset{H}{C}}-$$

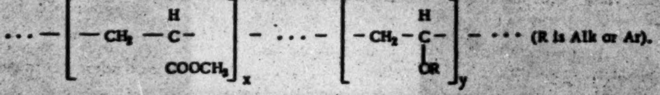
TABLE 1

Comparison of the Compositions of Copolymers of Vinyl Ethers with Methyl Methacrylate and with Methyl Acrylate

Name of residue	Molar percentage of methacrylate or acrylate residues in the copolymer containing the following residues		
	 $-CH_2-\underset{OC_2H_5}{\overset{H}{C}}-$	 $-CH_2-\underset{OC_4H_9}{\overset{H}{C}}-$	 $-CH_2-\underset{OC_6H_5}{\overset{H}{C}}-$
(Molar ratio of monomers 1:1)			
Methyl methacrylate	85.35	86.4	81.05
Methyl acrylate	71.8	67.3	72.4
(Molar ratio of monomers 1:3)			
Methyl methacrylate	78.35	76.33	65.38
Methyl acrylate	55.9	59.1	57.9

The course of the copolymerization of methyl acrylate with a vinyl ether can be represented as follows:

$$n\,CH_2{=}CHCOOCH_3 + m\,CH_2{=}CHOR \longrightarrow$$



$$\cdots-\left[-CH_2-\underset{COOCH_3}{\overset{H}{C}}-\right]_x-\cdots-\left[-CH_2-\underset{OR}{\overset{H}{C}}-\right]_y-\cdots \text{ (R is Alk or Ar).}$$

EXPERIMENTAL

The starting materials were freshly distilled and had the following constants:

Methyl acrylate: b. p. 80-81°; n_D^{20} 1.3780; d_4^{20} 0.9550.

Ethyl vinyl ether: b. p. 35.9°; n_D^{20} 1.3778; d_4^{20} 0.7533.

Butyl vinyl ether: b. p. 93.5-93.7°; n_D^{20} 1.4028; d_4^{20} 0.7791.

Phenyl vinyl ether: b. p. 155-156°; n_D^{20} 1.5225; d_4^{20} 0.9765.

Acetone: b. p. 56.5°; n_D^{20} 2.3595.

Methanol: b. p. 64-65°; n_D^{20} 1.3300.

Experimental Procedure. The copolymerization was carried out in sealed glass tubes at 60 ± 1°. Benzoyl peroxide was used as initiator, and the reaction components were taken in various molar ratios. Reaction proceeded continuously for forty hours, when solid or highly viscous products were obtained. When reaction was complete, the tubes were cooled to 0°. Control experiments on the polymerization of the individual starting materials were conductedunder the same conditions. The reaction products were brought into solution and reprecipitated, and were then extracted until there was no longer any reaction for double bonds. The products were then treated with selective solvents and dried to constant weight. The polymerization products were analyzed for carbon and hydrogen, and their compositions calculated.

In order to check the ability of the monomers to undergo free-radical polymerization, some control tests were made.

1. Experiments on the tendency of methyl acrylate to undergo polymerization in presence of benzoyl peroxide were carried out by the above-described procedure. In the first experiments reaction was very violent (with explosion), and the amount of benzoyl peroxide was therefore reduced to 0.05%. The duration of the polymerization was 40 hours. The methyl acrylate polymer was soluble in acetone, less soluble in benzene, and insoluble in methanol, ether, and water. Elementary analysis showed that the purified polymer contained the following amounts of carbon and oxygen:

Found %: C 55.76; 55.75; H 7.22; 7.24
Calculated %: C 55.80; H 7.00

2. Ethyl, butyl, and phenyl vinyl ethers were heated in presence of benzoyl peroxide for 40 hours. Fractionation yielded the original ethers, and an insignificant resinous residue remained at the bottom of the distilling flask.

I Copolymerization of Methyl Acrylate and Ethyl Vinyl Ether

The reactants were 7.13 g (0.083 mole) of methyl acrylate and 17.87 g (0.248 mole) of ethyl vinyl ether (molar ratio 1:3). The contents of the tube became highly viscous.

The copolymer was tested for solubility in various solvents, and it was found that it dissolved in methanol, but not in gasoline (b. p. 70-80°). It may be noted that polymethyl acrylate is insoluble in methanol. The dried copolymer was analyzed, accurate within 0.0001 g, for carbon and hydrogen contents. Also, by hydrolysis with alcoholic alkali, the content of methyl acrylate residues was determined. After precipitation of the copolymers, the solution was analyzed for its content of ethyl vinyl ether by iodometric titration, which showed the presence of 10.56 g of unchanged ethyl vinyl ether.

The copolymerization of methyl acrylate and ethyl vinyl ether was carried out also at other molar ratios by the procedure described above, with the exception that the amount of benzoyl peroxide was reduced to 0.05%, since the copolymerization was accompanied by an explosion when larger amounts were used. The monomer ratios, yields, and compositions of the copolymers are given in Table 2.

The compositions of the copolymers calculated from the elementary analysis is in accord with the results of the direct determination of methyl acrylate residues, which was carried out by hydrolysis of the copolymer in alcoholic alkali and subsequent back-titration of the alkali with acid.

The proportion of methyl acrylate residues, as calculated from the elementary analysis, is in satisfactory agreement with the value obtained by hydrolysis of the acrylate ester groups with alcoholic alkali.

TABLE 2

Yields and Compositions of Copolymers of Methyl Acrylate and Ethyl Vinyl Ether

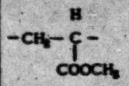
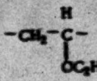
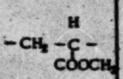
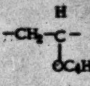
Proportions of monomers (mole-%)		Yield of polymer or copolymer (%)	Results of elementary analysis		Proportion of monomer residues in copolymer (mole-%)		Proportion of methyl acrylate residues in copolymer determined by hydrolysis (mole-%)
$CH_2=CHCOOCH_3$	$CH_2=CHOC_2H_5$		%C	%H	 $-CH_2-\underset{COOCH_3}{\overset{H}{C}}-$	 $-CH_2-\underset{OC_2H_7}{\overset{H}{C}}-$	
100	–	92	55.75	–	100	–	99.9
75	25	87.8	57.08 57.00	7.86 7.77	87.14	12.86	86.48
50	50	72.2	58.34 58.59	8.02 8.01	71.8	28.2	73.96
25	75	45.3	59.79 59.85	8.52 8.48	55.9	44.1	61.3
–	100	Nil	–	–	–	–	–

TABLE 3

Yields and Compositions of Copolymers of Methyl Acrylate and Butyl Vinyl Ether

Proportions of monomers (mole-%)		Yield of polymer or copolymer (%)	Results of elementary analysis		Proportion of monomer residues in copolymer (mole-%)		Proportion of methyl acrylate residues in copolymer determined by hydrolysis (mole-%)
$CH_2=CHCOOCH_3$	$CH_2=CHOC_4H_9$		%C	%H	 $-CH_2-\underset{COOCH_3}{\overset{H}{C}}-$	 $-CH_2-\underset{OC_4H_9}{\overset{H}{C}}-$	
100	–	92.0	55.76 55.75	7.22 7.24	100	–	99.02
75	25	86.84	58.46 58.54	7.88 7.89	84.9	15.1	81.78
50	50	72.0	61.76 61.51	8.91 8.90	67.3	32.7	61.75
25	75	39.2	62.96 62.68	9.35 9.21	59.1	40.9	53.59
–	100	Nil	–	–	–	–	–

II. Copolymerization of Methyl Acrylate and Butyl Vinyl Ether

The reactants were 5.56 g (0.0646 mole) of methyl acrylate and 19.44 g (0.194 mole) of butyl vinyl ether (molar ratio 1:3). The contents of the tube became very viscous. The copolymerization conditions are described above. The copolymer was tested for solubility in various solvents, and it was shown that the copolymer dissolved in acetone and was precipitated by gasoline (b. p. 70-80°). The copolymer was treated with gasoline until it no longer gave a reaction for double bonds. After being dried to constant weight, the copolymer was analyzed for carbon and hydrogen. The proportion of methyl acrylate residues in the copolymer was determined by hydrolysis with alcoholic alkali. The results of the analysis and the compositions of the copolymers are given in Table 3.

The solution remaining after the separation of the copolymer was analyzed by the iodometric method for its content of butyl vinyl ether [9]. The copolymerization of methyl acrylate and butyl vinyl ether was carried out also at other molar ratios. The yields and compositions of the copolymers are given in Table 3.

As a check on the method, the methyl acrylate ester groups were hydrolyzed by heating the polymer with alcoholic alkali. The excess of alkali was then back-titrated, and the proportion of ester groups was calculated. When the difference in the methods of determination is considered, the agreement between the results obtained must be regarded as satisfactory.

III. Copolymerization of Methyl Acrylate with Phenyl Vinyl Ether

The reactants were 4.9 g of methyl acrylate and 20.1 g of phenyl vinyl ether (molar ratio 1:3). The contents of the tube became very viscous. The copolymerization conditions are described above. The copolymers were dissolved in acetone and precipitated with methanol. They were then treated with methanol until the monomers had been completely removed. The copolymers were then dried to constant weight and analyzed for carbon and hydrogen. The compositions of the copolymers were calculated from these results. Analyses were made also for the contents of methyl acrylate residues, the ester groups being hydrolyzed by heating the polymer with alcoholic alkali.

The compositions of the copolymers calculated from the results of elementary analysis and determined directly were closely in agreement. The copolymerization of methyl acrylate and phenyl vinyl ether was carried out also for other concentrations of the original monomers. The yields and compositions of the copolymers and polymers are given in Table 4.

TABLE 4

Yields and Compositions of Copolymers of Methyl Acrylate and Phenyl Vinyl Ether

Proportions of monomers (mole %)		Yield of polymer or copolymer (%)	Results of elementary analysis		Proportion of monomer residues in copolymer (mole-%)		Proportion of methyl acrylate residues in copolymer determined by hydrolysis (mole-%)
$CH_2=CHCOOCH_3$	$CH_2=CHOC_6H_5$		%C	%H	$-CH_2-\underset{COOCH_3}{\overset{H}{C}}-$	$-CH_2-\underset{OC_6H_5}{\overset{H}{C}}-$	
100	–	92.0	57.75	7.20	100	–	–
75	25	77.6	60.65 60.45	6.61 6.57	85.1	14.9	79.8
50	50	58.8	64.03 64.33	6.93 7.09	72.4	27.6	64.04
25	75	33.2	67.98 67.93	6.91 6.68	57.9	42.1	49.30
–	100	Nil	–	–	–	–	–

The solutions remaining after separation of the copolymers were analyzed for the original monomers. Methyl acrylate was determined by hydrolysis with alcoholic alkali, the amount found being 0.28 g.

Phenyl vinyl ether was obtained by fractionation. First of all the organic solvents were driven off in presence of hydroquinone, and then the residue was treated with water, dried with potassium carbonate, and fractionated. A liquid was obtained having b. p. 154-155°, n_D^{20} 1.5220, and d_4^{20} 0.9758 (14.2 g). These constants correspond to phenyl vinyl ether [9]. Films obtained from the copolymer of methyl acrylate and phenyl vinyl ether were friable and had the rubberlike appearance that is characteristic of methyl acrylate polymers.

SUMMARY

1. The conditions required for the copolymerization of methyl acrylate with ethyl, butyl, and phenyl vinyl ethers have been studied. Copolymers of methyl acrylate with ethyl, butyl, and phenyl vinyl ethers have been prepared.

2. It has been shown that the composition of the copolymer obtained depends on the concentrations of vinyl ether and methyl acrylate in the given reation mixture.

3. Copolymers of methyl acrylate with vinyl ethers contain greater molar proportions of the latter than the copolymers of methyl methacrylate with the same vinyl ethers.

Received December 23, 1953

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

LITERATURE CITED

[1] M. F. Shostakovsky and A. M. Khomutov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, No. 6, 1049.*

[2] M. F. Shostakovsky and A. M. Khomutov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 2, 323.**

[3] M. F. Shostakovsky, I. A. Chekulaeva, and A. M. Khomutov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 3, 484.***

[4] M. F. Shostakovsky and A. M. Khomutov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 5, 924.

[5] M. F. Shostakovsky and A. M. Khomutov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 5, 924.

[6] V. V. Markovnikov, Material Relating to the Mutual Effects of Atoms in Chemical Compounds, Kazan Univ. Press, 1869, p. 50.

[7] E. R. Blout and H. Mark, Monomers, Interscience Publishers, N.Y., p. 43.

[8] S. N. Ushakov, S. P. Mintsinger, and G. A. Shtraikhmon, Prog. Chem., 19, 3, 278 (1950).

[9] M. F. Shostakovsky, Vinyl Ethers, Acad. Sci. USSR Press, 1952, p. 87.

---

* See Consultants Bureau Translation, page 931.

** " " " " , page 263.

*** " " " " , page 411.

**** " " " "

***** " " " "

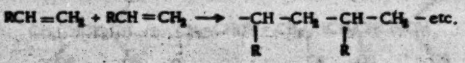
POLYMERIZATION OF VINYL COMPOUNDS

COMMUNICATION 1. STEPWISE SYNTHESIS OF POLY [BUTYL VINYL ETHER]

M. F. Shostakovsky and V. A. Gladyshevskaya

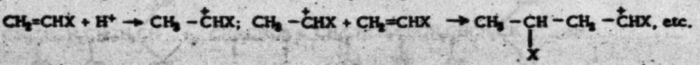
Our previous investigations have shown that the polymerization reactions of alkyl vinyl ethers proceed by a chain mechanism [1, 2]. We have found recently, however, that under certain conditions alkyl vinyl ethers may polymerize in a stepwise manner [3].

The distinguishing feature of free-radical and ionic chain reactions is the formation of macromolecular compounds whatever the duration of the reaction may be, without formation of products of low molecular weight (dimers, trimers, etc.). Free-radical chain polymerization occurs by the opening of double bonds and the subsequent uniting of the molecules according to the following scheme [4]:



$$RCH{=}CH_2 + RCH{=}CH_2 \longrightarrow -\underset{R}{\underset{|}{C}H}-CH_2-\underset{R}{\underset{|}{C}H}-CH_2-\text{etc.}$$

Polymerization by the ionic chain mechanism may be represented as follows [2].



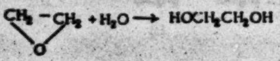
$$CH_2{=}CHX + H^+ \rightarrow CH_3-\overset{+}{C}HX;\ CH_3-\overset{+}{C}HX + CH_2{=}CHX \rightarrow CH_3-\underset{X}{\underset{|}{C}H}-CH_2-\overset{+}{C}HX,\ \text{etc.}$$

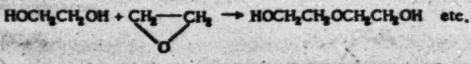
Chain polymerization of alkyl vinyl ethers provides an excellent synthetic method for the preparation of macromolecular products of any degree of complexity.

The stepwise form of ionic polymerization is of special interest because it permits the preparation of the simplest polymerization products, namely the dimers, trimers, etc. With the aid of these we can study the direction of the addition of the monomers and the structure of the terminal units, and we can determine also the variation in chemical and physical properties as we pass from the monomer to the n-mers.

The characteristic features of stepwise polymerization are, first, the presence of an end group, and second, the transfer of hydrogen atoms or of whole groups as each new molecule of monomer adds [4, 5]. Stepwise polymerization is facilitated by compounds containing mobile hydrogen, such as water, alcohol, etc.

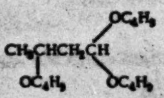
These compounds can play various parts, for they may catalyze the process and may take part in the formation of the terminal units. The presence of traces of water, for example, is sufficient to bring about the polymerization of ethylene oxide, which is very stable in the dry state. The polymerization of ethylene oxide may be presented as follows [6]:



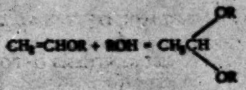


i.e. the process proceeds stepwise.

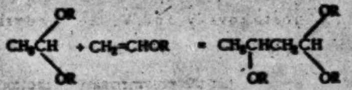
When studying the behavior of mixtures of butyl vinyl ether and butyl alcohol in a polymerization process, in addition to polymer we isolated 1,1,3-tributoxybutane [3]:



The presence of 1,1,3-tributoxybutane among the reaction products suggested to us that under certain conditions, i.e. when an alcohol is present, the polymerization of an alkyl vinyl ether is stepwise. The alcohol reacts with the alkyl vinyl ether, and the resulting acetal reacts with more of the ether, yielding 1,1,3,-tributoxybutane:

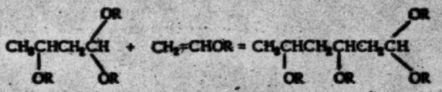


$$CH_2{=}CHOR + ROH = CH_3CH\begin{array}{l}OR\\OR\end{array} \qquad (1)$$

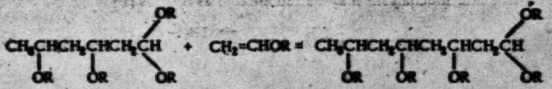


$$CH_3CH\begin{array}{l}OR\\OR\end{array} + CH_2{=}CHOR = CH_3\underset{OR}{CH}CH_2CH\begin{array}{l}OR\\OR\end{array} \qquad (2)$$

The synthesis of acetals from vinyl ethers (Equation 1) is well known and is described in a paper by Shostakovsky and Gershtein [7]. We have carried out the reaction of Equation 2 (the reaction of acetaldehyde dibutyl acetal with butyl vinyl ether) for the specific purpose of explaining the presence of 1,1,3-tributoxybutane in the products of the polymerization of butyl vinyl ether in presence of butyl alcohol [3]. Also, by reaction between 1,1,3-tributoxybutane and butyl vinyl ether it is possible to carry the reaction further with gradual increase in the complexity of the molecule:



$$CH_3\underset{OR}{CH}CH_2CH\begin{array}{l}OR\\OR\end{array} + CH_2{=}CHOR = CH_3\underset{OR}{CH}CH_2\underset{OR}{CH}CH_2CH\begin{array}{l}OR\\OR\end{array} \qquad (3)$$



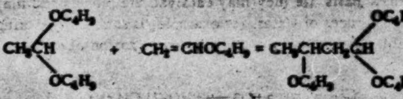
$$CH_3\underset{OR}{CH}CH_2\underset{OR}{CH}CH_2CH\begin{array}{l}OR\\OR\end{array} + CH_2{=}CHOR = CH_3\underset{OR}{CH}CH_2\underset{OR}{CH}CH_2\underset{OR}{CH}CH_2CH\begin{array}{l}OR\\OR\end{array} \quad \text{etc.} \qquad (4)$$

i.e. the dimer, trimer, and so on are formed successively with already formed end groups. We assume that the end group is an acetal grouping, which is formed, as shown above, by the addition of an alcohol at the double bond.

In order to confirm this view, in the present investigation we have synthesized poly[butyl vinyl ether] having various degrees of polymerization. The first stage consisted in the reaction of acetaldehyde dibutyl acetal with butyl vinyl ether. A similar reaction has been described by Hoaglin and Hirsh [8]. The butoxy compounds so obtained reacted in the successive stages of the reaction with alkyl vinyl ethers.

We have carried out the following syntheses:

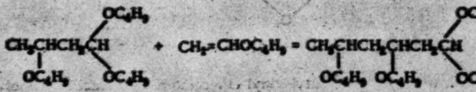
1) Synthesis of 1,1,3-tributoxybutane:



$$CH_3CH\begin{array}{l}OC_4H_9\\OC_4H_9\end{array} + CH_2{=}CHOC_4H_9 = CH_3\underset{OC_4H_9}{CH}CH_2CH\begin{array}{l}OC_4H_9\\OC_4H_9\end{array}$$

(I)

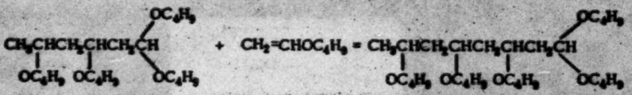
2) Synthesis of 1,1,3,5-tetrabutoxyhexane:



$$CH_3\underset{OC_4H_9}{CH}CH_2CH\begin{array}{l}OC_4H_9\\OC_4H_9\end{array} + CH_2{=}CHOC_4H_9 = CH_3\underset{OC_4H_9}{CH}CH_2\underset{OC_4H_9}{CH}CH_2CH\begin{array}{l}OC_4H_9\\OC_4H_9\end{array}$$

(II)

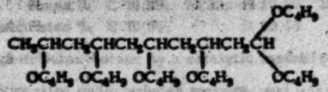
3) Synthesis of 1,1,3,5,7-pentabutoxyoctane:



$$CH_3\underset{OC_4H_9}{CH}CH_2\underset{OC_4H_9}{CH}CH_2CH\begin{array}{l}OC_4H_9\\OC_4H_9\end{array} + CH_2{=}CHOC_4H_9 = CH_3\underset{OC_4H_9}{CH}CH_2\underset{OC_4H_9}{CH}CH_2\underset{OC_4H_9}{CH}CH_2CH\begin{array}{l}OC_4H_9\\OC_4H_9\end{array}$$

(III)

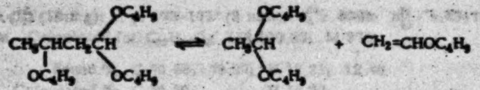
It was shown also that the reaction products (I), (II), and (III) react further with the original butyl vinyl ether and yield still more complex compounds containing the appropriate numbers of butoxyl groups. Thus, in the synthesis of 1,1,3-tributoxybutane some 1,1,3,5-tetrabutoxyhexane was obtained; in the synthesis of 1,1,3,5-tetrabutoxyhexane, some 1,1,3,5,7-pentabutoxyoctane was obtained; and in the synthesis of 1,1,3,5,7-pentabutoxyoctane, a very small fraction (0.6 g) of b.p. 215-220° (3 mm) and n_D^{20} 1.4520 was obtained. It may be assumed that this fraction contained the compound 1,1,3,5,7,9-hexabutoxydecane:



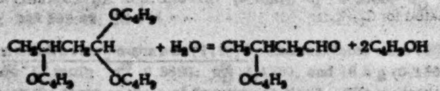
It was not found possible, however, to isolate compounds of higher molecular weight in the pure state, since they decomposed when distilled.

The yields of the compounds formed in these syntheses depend on many of the experimental conditions, particularly the proportion of the reactants. The highest yield of the main product of the synthesis was obtained when the molecular proportions of acetal and vinyl ether were 2:1.

It should be noted that, when the butoxy compounds are repeatedly distilled, they decompose into the original components, so that the processes of polymerization and depolymerization can be represented as follows:



The presence of terminal acetal groups in the synthesized butoxy compounds was established by hydrolysis:



The aldehyde formed was determined quantitatively by the bisulfite method [9]. It was found that the conditions required for the hydrolysis of (I), (II), and (III) were not the same: as the molecular weight rises, milder conditions are needed for the hydrolysis.

EXPERIMENTAL

1. Synthesis of 1,1,3-Tributoxybutane (I). The starting materials were:

a) Acetaldehyde dibutyl acetal, prepared by the condensation of butyl vinyl ether with butyl alcohol in presence of HCl as catalyst [7]. B. p. 185-186° (760 mm); d_4^{20} 0.8263; n_D^{20} 1.4085.

b) Butyl vinyl ether, prepared by the usual method [10]. B. p. 93-94° (760 mm); d_4^{20} 0.7790; n_D^{20} 1.4020.

A 5% solution of ferric chloride in butyl alcohol was used as catalyst.

A mixture of 174 g (1 mole) of the dibutyl acetal and 4 g of a 5% solution of ferric chloride in butyl alcohol was warmed to 48-50° and stirred while 50 g (0.5 mole) of butyl vinyl ether was added dropwise. The rate of addition was controlled so the temperature remained at 48-50°. When the whole of the ether had been added, reaction was allowed to continue for one hour, and the catalyst was then precipitated by anhydrous sodium carbonate powder (4 g). The mixture was stirred for three hours, and then filtered. A colorless liquid (215 g) was obtained. On being fractionated under reduced pressure, it yielded

Fraction I	B. p. .... 67-68° (8mm);	126 g
Fraction II	B. p. .... 70-135° (5 mm);	2.4 g
Fraction III	B. p. .... 133-135° (3 mm);	62.3 g
Fraction IV	B. p. .... 136-173° (3 mm);	1.2 g
Fraction V	B. p. .... 173-176° (3 mm);	6.6 g
Residue		12.6 g

The intermediate fractions (II and IV) were not investigated because of their small amount.

Refractionation of Fraction I at atmospheric pressure yielded, as the main fraction, acetaldehyde dibutyl acetal, b. p. 184-185° (760 mm): d_4^{20} 0.8259; n_D^{20} 1.4087. The literature [7] gives b. p. 185-186° (760 mm): d_4^{20} 0.8268; n_D^{20} 1.4085.

A second vacuum distillation of Fraction III yielded 1,1,3-tributoxybutane (I), b. p. 134-135° (3 mm): d_4^{20} 0.8655; n_D^{20} 1.4255; MR 81.02; M 266, 262; viscosity 3.573 centipoise. Calculated for $C_{16}H_{34}O_3$ MR 81.017; M 274.

Found %: C 70.09; 70.33; H 12.57, 12.44

$C_{16}H_{34}O_3$. Calculated %: C 70.00; H 12.49

We have previously prepared 1,1,3-tributoxybutane by a catalytic method [3].

Fraction V was purified by refractionation under reduced pressure, and was found to be 1,1,3,5-tetrabutoxyhexane (II), b. p. 175-177° (3 mm); d_4^{20} 0.8886; n_D^{20} 1.4345; MR 109.88; M 365, 360. Calculated for $C_{22}H_{46}O_4$: MR 109.83; M 374.

2. Synthesis of 1,1,3,5-Tetrabutoxyhexane (II). The reactants were 92 g (0.335 mole) of 1,1,3-tributoxybutane, b.p. 134-135° (3 mm); d_4^{20} 0.8658; n_D^{20} 1.4262, and 11 g (0.11 mole) of butyl vinyl ether. The reaction conditions were the same as those of Experiment No. 1.

The product was 98 g of a slightly colored liquid, which was repeatedly distilled under reduced pressure. As a result, in addition to unchanged 1,1,3-tributoxybutane, the following compounds were obtained:

a) 1,1,3,5-Tetrabutoxyhexane (II) (12.8 g); b. p. 173-175° (3 mm); d_4^{20} 0.8892; n_D^{20} 1.4347; MR 109.57; M 360, 357; viscosity 8.374 centipoise. Calculated for $C_{22}H_{46}O_4$: MR 109.83; M 374

Found %: C 70.66; 70.27; H 12.31; 12.40

$C_{22}H_{46}O_4$ Calculated %: C 70.50; H 12.37

b) 1,1,3,5,7-pentabutoxyoctane (III) (8.3 g); b.p. 195-197° (3 mm); d_4^{20} 0.9033; n_D^{20} 1.4435; MR 139.28; M 467, 463. Calculated for $C_{28}H_{58}O_5$: MR 139.42; M 474.

3. Synthesis of 1,1,3,5,7-Pentabutoxyoctane (III). The reactants were 125 g (0.334 mole) of 1,1,3,5-tetrabutoxyhexane, b.p. 174-175° (3 mm); d_4^{20} 0.8890; n_D^{20} 1.4350, and 16.5 g (0.165 mole) of butyl vinyl ether. The reaction conditions were the same as those of Experiment No. 1. The product was 135 g of a slightly colored viscous liquid, which was distilled repeatedly under reduced pressure. As a result, in addition to unchanged 1,1,3,5-tetrabutoxybutane (91.8 g), 21.8 g of 1,1,3,5,7-pentabutoxyoctane (III) was isolated. It had b.p. 195-197° (3 mm); d_4^{20} 0.9032; n_D^{20} 1.4440; MR 139.60; M 484, 481; viscosity 18.827 centipoise. Calculated for $C_{28}H_{58}O_5$: MR 139.42; M 474.

Found %: C 70.35; 70.69; H 12.19; 11.97

$C_{28}H_{58}O_5$ Calculated %: C 70.83; H 12.31

In an attempt to fractionate the material remaining after the separation of 1,1,3,5,7-pentabutoxyoctane under reduced pressure, we succeeded in obtaining 0.6 g of a substance of b.p. 215-220° (3 mm); n_D^{20} 1.4520. It was not possible to examine this further owing to the small amount and its very high boiling point. It may be assumed that 1,1,3,5,7,9-hexabutoxydecane was present in this fraction.

4. Hydrolysis of the Butoxy Compounds. A small sealed tube containing a weighed amount (0.03-0.04 g) of the substance was introduced into a flask containing 20 ml of 0.2 N sodium bisulfite. The tube was then broken by shaking the flask vigorously. After a certain period of time, the length of which depended on the structure of the butoxy compound, the excess of bisulfite was titrated. For 1,1,3,5,7-pentabutoxyoctane the titration was carried out immediately after the addition of the compound to the bisulfite solution, for 1,1,3,5-tetrabutoxyhexane the titration was carried out after 30 minutes, and for 1,1,3-tributoxybutane it was carried out after one hour.

In each case a control experiment was carried out at the same time. The degree of hydrolysis of the butoxy compound was calculated by the following formula [9]:

$$x = \frac{M(a - b)}{200\,p}\ \%\ \text{of the theoretical value}$$

($\underline{a}$ is the volume of 0.1 N iodine used in the control titration (ml); $\underline{b}$ is the volume of 0.1 N iodine required for the titration of the unchanged bisulfite (ml); $\underline{p}$ is the weight of substance (g); and $\underline{M}$ is the molecular weight of the butoxy compound).

The results on the hydrolysis of the butoxy compounds are given in the table.

TABLE 1

Hydrolysis of the Butoxy Compounds

Butoxy compound	Hydrolysis, %
1,1,3-Tributoxybutane	96.0
	96.5
1,1,3,5-Tetrabutoxyhexane	97.2
	96.8
1,1,3,5,7-Pentabutoxyoctane	97.6
	96.9

SUMMARY

1. The stepwise synthesis has been demonstrated of pure substances of various degrees of complexity corresponding to various stages in the synthesis of poly(butyl vinyl ether).

2. The following substances have been isolated and characterized: 1,1,3-tributoxybutane, 1,1,3,5-tetrabutoxyhexane, and 1,1,3,5,7-pentabutoxyoctane.

Received December 23, 1953

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

LITERATURE CITED

[1] M. F. Shostakovsky, Investigations on Macromolecular Compounds, Acad. Sci. USSR Press, Moscow, 1949.

[2] M. F. Shostakovsky, Vinyl Ethers, Acad. Sci. USSR Press, Moscow, 1952.

[3] M. F. Shostakovsky and V. A. Gladyshevskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 2, 362.*

[4] V. V. Korshak, Monograph "Chemistry of Macromolecular Compounds", Acad. Sci. USSR Press, Moscow, 1950.

[5] H. Staudinger, Macromolecular Organic Compounds, United Sci. Tech. Press. Theoretical Chemistry Series, Leningrad, 1935.

[6] I. P. Losev and G. S. Petrov, Chemistry of Synthetic Resins, State Chem. Press, Moscow, 1951.

[7] M. F. Shostakovsky and N. A. Gershtein, J. Gen. Chem., 16, 937 (1946).

[8] R. Hoaglin and D. Hirsh, J. Am. Chem. Soc. 10, 3468 (1949).

[9] M. F. Shostakovsky and E. N. Prilezhaeva, J. Gen. Chem., 17, 6 (1947).

[10] A. E. Favorsky and M. F. Shostakovsky, J. Gen. Chem., 13, 1 (1943).

---

* See Consultants Bureau Translation, p. 299.

SYNTHESIS AND REACTIONS OF VINYL ETHERS OF ETHANOLAMINES

COMMUNICATION 6. VINYL ETHER OF 2-ANILINOETHANOL

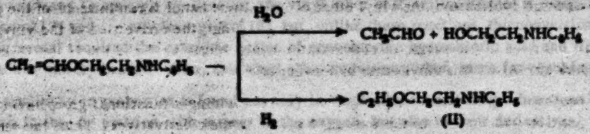
M. F. Shostakovsky and I. A. Chekulaeva

A comparative study of the synthesis and reactions of some vinyl ethers of ethanolamines [1, 2, 3] has shown that the vinylation of amino alcohols demands different conditions from those used for unsubstituted aliphatic alcohols. The vinylation products also differ greatly. It was therefore of interest to study the relation between structure and properties for 2-anilinoethanol and its vinyl ether.

Vinylation of 2-anilinoethanol in presence of its potassium derivative as catalyst gave an 83-85% yield of the vinyl ether:

$$C_6H_5NHCH_2CH_2OH + HC\equiv CH \rightarrow \underset{(I)}{CH_2{=}CHOCH_2CH_2NHC_6H_5}$$

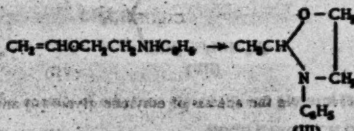
When caustic potash was used as catalyst, the yield of vinyl ether was only 47-50%, being reduced on account of much resinification of the reaction products. The presence of solvent had no appreciable effect on the vinylation reaction. It was found that 2-anilinoethanol is not so readily vinylated as unsubstituted aliphatic alcohols [4], but the replacement of a hydrogen atom by a phenyl radical in the amino group of 2-aminoethanol or 2-diethylaminoethanol results in increased reactivity [1, 2]. In order to prove its structure, the vinyl ether of 2-anilinoethanol was subjected to hydrolysis and to hydrogenation, when the following reactions occurred:



$$CH_2{=}CHOCH_2CH_2NHC_6H_5 \xrightarrow{H_2O} CH_3CHO + HOCH_2CH_2NHC_6H_5$$

$$CH_2{=}CHOCH_2CH_2NHC_6H_5 \xrightarrow{H_2} \underset{(II)}{C_2H_5OCH_2CH_2NHC_6H_5}$$

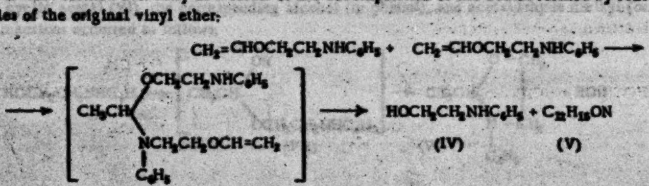
It was found that the vinyl ether of 2-anilinoethanol, unlike the vinyl ethers of other amino alcohols [1, 2, 3], is converted into a cyclic acetal in presence of traces of concentrated hydrochloric acid:



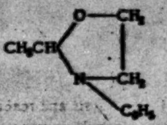
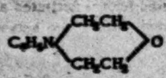
(III)

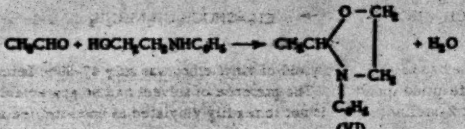
According to the literature [5], cyclization of the vinyl ether of 2-anilinoethanol occurs also when the corresponding amino alcohol is vinylated in presence of cadmium or zinc acetate as catalyst.

When the vinyl ether of 2-anilinoethanol was allowed to react in presence of hydrochloric acid, 2-anilinoethanol (IV) and a substance of composition $C_{22}H_{18}ON$ (V) were isolated in addition to the cyclic acetal. These two substances were formed evidently as a result of the decomposition of the acetal formed by reaction between two molecules of the original vinyl ether:



Owing to the readiness with which reactions of this sort occurred, the vinyl ether of 2-anilinoethanol did not unite with alcohols. The synthesis of an acetal from this vinyl ether and an alcohol could not be effected even when heat was applied. The only result was an increase in the yields of 2-anilinoethanol and the compound (V).

The structure of the cyclic acetal (III), which has not been described in the literature, was proved first by hydrolysis with 2% sulfuric acid, which occurred readily and completely at room temperature. The ease of hydrolysis confirmed the oxazolidine structure of the acetal [6]  and showed that the morpholine ring  must be absent. Second, the properties of this acetal were compared with those of 2-methyl-3-phenyloxazolidine (VI), which was prepared by reaction between acetaldehyde and 2-anilinoethanol:

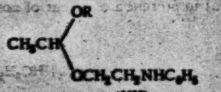


(VI)

This reaction yielded a product of quite definite structure, and it had the same physical and chemical properties as the acetal (III).

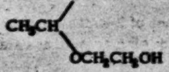
In its tendency to undergo cyclization, the vinyl ether of 2-anilinoethanol is reminiscent of the partial vinyl ethers of glycerol [7] and ethylene glycol [8], but, unlike these reactions, the conversion of the vinyl ether (I) into its cyclic acetal required the catalytic action of concentrated hydrochloric acid and would not take place when the substance was merely heated. Also, this vinyl ether underwent other, more far-reaching changes.

This similarity in properties is found not only in vinyl ethers containing a functional group having a mobile hydrogen atom in the β- position with respect to the oxygen, but also in their derivatives. Thus, the amino acetal of structure

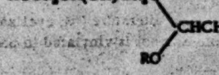


(VII)

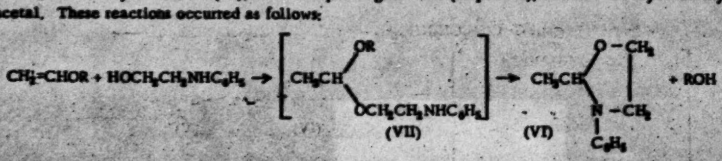
also tends to form cyclic products, like the acetals of ethylene glycol [9] and glycerol [10]:



and



Owing to the instability of the amino acetal (VII) under the conditions of the synthesis, we were unable to isolate it by the action of a vinyl ether on 2-anilinoethanol. Only the products of its further reaction were obtained, i.e. the cyclic acetal (VI), the corresponding alcohol (or phenol), and acetaldehyde dialkyl (or diaryl) acetal. These reactions occurred as follows:



(VII) (VI) (1)

$$ROH + CH_2{=}CHOR \longrightarrow CH_3CH(OR)_2 \quad (2)$$

These reactions were studied in some detail for butyl vinyl and phenyl vinyl ethers.

Among other reactions of the vinyl ether of 2-anilinoethanol, its polymerization was studied. It was found that it would polymerize in presence of 2,2'-azobis[2-methylpropionitrile], but not in presence of ferric chloride and concentrated hydrochloric acid (in the presence of concentrated hydrochloric acid the vinyl ether undergoes other changes, as described above).

EXPERIMENTAL*

1. Synthesis of the Vinyl Ether of 2-Anilinoethanol (I)

2-Anilinoethanol was prepared from aniline and ethylene oxide [11] and had the following constants: b. p. 135° (3 mm); n_D^{20} 1.5798; d_4^{20} 1.0947.

The potassium derivative of 2-anilinoethanol, which was used as a catalyst, was prepared by heating the amino alcohol with potassium at 60-70°. A mixture of 75.5 g of 2-anilinoethanol, 8.3 g of its potassium derivative, and 150 ml of benzene was placed in a steel 2.5-liter autoclave. Acetylene was blown through for a time and then passed in up to a pressure of 14-16 atm. The autoclave was heated to 140-150° and maintained at that temperature for 4-6 hours. The reaction products were vacuum-fractionated, and after removal of benzene the following fractions were collected:

Fraction I	56-117° (7 mm);	n_D^{20} 1.5510;	3.0 g
Fraction II	117-122° (7 mm);	n_D^{20} 1.5530;	85.0 g
Resin			11.4 g

When Fractions I and II were treated with sodium and redistilled, 82.2 g (83.0%) of the vinyl ether of 2-anilinoethanol was obtained. It was a thick colorless liquid, soluble in acetone, benzene, ethanol, and other alcohols, but insoluble in water. It turned yellow when allowed to stand in the air. Its constants were b.p. 116-116.5° (6 mm); 108-109° (3.5 mm); n_D^{20} 1.5523; d_4^{20} 1.0295; MR 50.67; M (cryoscopically in benzene) 151.4; 151.2; Calculated for $C_{10}H_{13}ON$. MR 49.53; M 163.2.

The exaltation of the molecular refraction of the vinyl ether of 2-anilinoethanol and of its derivatives can evidently be explained by the presence of the phenyl radical.

Found %: C 73.38; 73.36; H 8.24; 8.16; N 8.78, 8.80
$C_{10}H_{13}ON$. Calculated %: C 73.59; H 8.03; N 8.57

The literature gives: b. p. 128-132° (9 - 10 mm) [5]; b. p. 130-133° (10 mm) [12].

Similar experiments on the vinylation of 2-anilinoethanol were carried out with caustic potash as catalyst, with and without solvent. The results are given in Table 1.

TABLE 1

Dependence of the Yield of the Vinyl Ether of 2-Anilinoethanol on the Vinylation Conditions

Expt. No.	Catalyst (10% on the weight of 2-anilinoethanol)	Solvent	Percent yield of crude vinyl ether (b.p. 117-122°/7 mm)	Resin (% of wt. of aminoalcohol)
1	Potassium derivative	Benzene	83 - 85	13 - 15
2	Caustic potash	Benzene	47 - 50	40 - 45
3	Caustic potash	No solvent	45 - 50	45 - 50

The vinyl ether of 2-anilinoethanol was readily hydrolyzed by 2% sulfuric acid at room temperature. The acetaldehyde so obtained was determined quantitatively by the bisulfite method [13], and the values found for the content of vinyl ether were 98.8 and 98.9%.

Hydrogenation of the vinyl ether (I) over Raney nickel at 120° in an autoclave yielded the ethyl ether of 2-anilinoethanol (II), a thick colorless liquid, b. p. 107-108° (4 mm); n_D^{20} 1.5360; d_4^{20} 1.0002; MR 51.49; calculated for $C_{10}H_{15}ON$ MR 50.02.

Found %: C 72.65; 73.01; H 9.11; 9.07; N 8.58; 8.71
$C_{10}H_{15}ON$. Calculated %: C 72.70; H 9.15 N 8.47

---

* M. P. Starshinova, a student of Irkutsk University, assisted in the experimental work.

The literature gives: b. p. 132-136° at 14 mm [12]; b. p. 262-263°; d_{20}^{20} 1.0156 [14].

The polymerization of the vinyl ether in presence of 2,2'-azobis[2-methylpropionitrile] (2% on the weight of the ether) was carried out in a sealed glass tube, which was held continuously at 60-65° for 100 hours. The polymer was separated from unchanged vinyl ether by vacuum distillation. The yield of polymer was 10.4-10.7%; it was a dark-red viscous mass, soluble in ether, benzene, acetone, and alcohols; M (cryoscopically in benzene) 561, 501.

Found %: N 8,85; 8.51
$C_{10}H_{13}ON$. Calculated %: N 8.57

2. Reaction of the Vinyl Ether of 2-Anilinoethanol with Alcohols

The reaction was carried out in a round-bottomed flask fitted with stirrer, thermometer, and reflux condenser. When two drops (0.06 g) of concentrated hydrochloric acid were added to a mixture of 18.5 g (0.113 mole) of the vinyl ether of 2-anilinoethanol and 33,7 g (0.455 mole) of butyl alcohol (b.p. 116-117°; n_D^{20} 1.3990), the temperature rose from 12° to 20°, and it was maintained at this value for three hours. The reaction mixture thickened and became violet in color. The reaction products were vacuum-fractionated:

Fraction I	b.p.	28-31° (3.5 mm);	26.4 g
Fraction II	b.p.	113-135° (6 mm);	9.9 g
Fraction III	b.p.	137-145° (6 mm);	4.4 g
Material collected in trap			6.3 g
Solid residue			4.9 g

Distillation of Fraction I and of the material collected in the trap yielded 32.4 g of butyl alcohol. Refractionation of Fractions II and III under reduced pressure yielded 1.1 g (6% on the amount of vinyl ether taken) of the cyclic acetal (III) and a mixture of 2-anilinoethanol and its vinyl ether.

In order to purify it, the acetal (III) was recrystallized twice from methanol and vacuum-dried (3-5 mm) at 30°, when some of it sublimed, yielding colorless crystals, m.p. 58.5-59.0°; M (crysoscopically in benzene) 160.5; 161.5. Calculated for $C_{10}H_{13}ON$ M 163.2.

Found %: C 73,49; 73.49; H 8,06; 8,01; N 8.52; 8.60
$C_{10}H_{13}ON$. Calculated %: C 73.59; H 8.02; N 8.57

The acetal was found to be soluble in alcohol, ether, benzene, and acetone, and it was readily hydrolyzed by 2% sulfuric acid at room temperature. The acetaldehyde formed in this way was determined quantitatively by the bisulfite method. The results for the content of acetal were 99.44%, 101.0%.

In order to prove the structure of the acetal (III), a mixture melting-point test was done for the acetal and 2-methyl-3-phenyloxazolidine (VI), which was prepared by mixing equimolecular amounts of acetaldehyde and 2-anilinoethanol under cooling. The resulting colorless crystals were purified by recrystallizing them twice from methanol; they melted at 59-59.5°. Hydrolysis with 2% sulfuric acid again went readily and completely, and values of 99.26% and 99.80% were found for the content of 2-methyl-3-phenyloxazolidine. A mixture of the compounds (III) and (VI) melted at 58-59°.

In order to resolve the mixture of 2-anilinoethanol and its vinyl ether, it was treated with gasoline (b.p. 50-100°), which extracted the vinyl ether. Distillation of the residue yielded 1.5 g (9.6% on the amount of the vinyl ether taken) of 2-anilinoethanol (IV), b.p. 132.5° (3 mm) $n_D^{22.5}$ 1.5786.

Found %: C 69,81; 70.01; H 8.18; 8,08; N 10.24; 10.14
$C_8H_{11}ON$. Calculated %: C 70.07; H 8.03 N 10.20

The solid residue from the first fractionation of the reaction mixture was dissolved in acetone and reprecipitated with petroleum ether (b.p. 30-50°). Vacuum drying (3-5 mm) yielded 4.6 g (21.4% on the amount of the vinyl ether taken) of a substance that corresponded, according to its analysis, to the compound $C_{12}H_{15}ON$. It was a brown powder of m.p. 96-98°, soluble in acetone, alcohol, and dioxane.

Found %: C 76.44; 76.33; H 8.06; 8.03; N 7.18; 7.17
$C_{12}H_{15}ON$. Calculated %: C 76.16; H 7.98; N 7.40

The reaction of the vinyl ether of 2-anilinoethanol with alcohols was studied also for the alcohol 2-anilinoethanol under various conditions. The behavior of the vinyl ether (I) in presence of concentrated hydrochloric acid was investigated also in absence of alcohols. The experimental results are given in Table 2.

TABLE 2

Effect of Concentrated Hydrochloric Acid on the Vinyl Ether of 2-Anilinoethanol in Presence and in Absence of Alcohols

Expt. No.	Alcohol	Composition of original mixture (g)		Initial and maximum reaction temperatures (°C)	Duration of reaction (hours)	Yield of reaction products		
		alcohol	vinyl ether			cyclic acetal (III)	the compound $C_{12}H_{15}ON$ (V)	2-anilino ethanol (IV)
						% on amount of ether taken		
1	Without alcohol	–	17.2	20/34	6	5.8	20.0	10.0
2	Without alcohol	–	28.0	100/230	5	13.2	31.2	42.5
3	Butyl alcohol	33.7	18.5	12/20	3	6.0	21.4	9.6
4	Butyl alcohol	30.6	67.5	90/116	27	6.8	25.6	12.8
5	2-Anilinoethanol	26.0	31.0	100/150	4	9.3	21.2	–*

3. Reactions of Alkyl Vinyl Ethers with 2-Anilinoethanol

The rections of 2-anilinoethanol (b.p. 131.5-132° (3 mm); $n_D^{18.5}$ 1.5800) with alkyl vinyl ethers was carried out in a round-bottomed flask fitted with stirrer, thermometer, and reflux condenser.

a) Reaction of Butyl Vinyl Ether with 2-Anilinoethanol in presence of Concentrated Hydrochloric Acid. Concentrated hydrochloric acid (two drops, i.e. 0.06 g) was added to a mixture of 23.2 g (0.23 mole) of butyl vinyl alcohol (b.p. 93-94°; $n_D^{18.5}$ 1.4025) and 31.7 g (0.23 mole) of 2-anilinoethanol. In the course of one hour the temperature rose from 18° to 28°, and it was maintained at this temperature for 90 minutes. The thick brown reaction mass was vacuum-fractionated, and the following fractions were obtained:

Fraction I B.p. . . . . 30 - 50° (4.5 mm); 8.7 g
Fraction II B.p. .108 - 140° (4.5 mm); 11.3 g
Fraction III B.p. .140 - 142° (4.5 mm); 20.8 g
Material collected in trap . . . . 6.4 g
Solid resin . . . . 7.5 g

Fraction I and the material in the trap were distilled at atmospheric pressure, and yielded:

1) 6.4 g of butyl vinyl ether;

2) 6.5 g (39.2% on the amount of the ether taken) of butyl alcohol, b.p. 116-118°; n_D^{19} 1.4000;

3) 1.1 g of acetaldehyde dibutyl acetal $CH_3CH(OC_4H_9)_2$: b.p. 180-184°; n_D^{19} 1.4088. The acetal was hydrolyzed with 2% sulfuric acid, and the aldehyde liberated was determined by the bisulfite method. The values found for the acetal content were 95.9% and 97.0%. The literature [16] gives b.p. 184-185° (760 mm) and n_D^{20} 1.4090.

Vacuum distillation of Fractions II and III yielded 5.0 g (13.2% on the amount of the ether taken) of 2-methyl-3-phenyloxazolidine (VI), b.p. 57.5-58.5° (see the previous experiment) and 24 g of unchanged 2-anilinoethanol. None of the desired acetal $CH_3CH\begin{cases}OC_4H_9\\OCH_2CH_2NHC_6H_5\end{cases}$ was isolated.

b) Reaction of Phenyl Vinyl Ether with 2-Anilinoethanol in presence of Concentrated Hydrochloric Acid at 95-100°: Concentrated hydrochloric acid (two drops, i.e. 0.06 g) was added to a hot (94°) mixture of 36.7 g (0.30 mole) of phenyl vinyl ether (b.p. 155-156°; $n_D^{19.6}$ 1.5228) and 42.0 g (0.30 mole) of 2-anilinoethanol. A temperature of 95-100° was maintained for 20 hours. The thick dark-brown reaction mass was vacuum-distilled, and the following fractions were collected:

---

* 2-Anilino ethanol, in quantity of 31.7 g.

Fraction I	B.p.	40°	(3 mm);	30.3 g
Fraction II	B.p.	40 - 110°	(3 mm);	2.8 g
Fraction III	B.p.	110 - 135°	(3 mm);	38.6 g
Material collected in trap				1.0 g
Solid resin				5.4 g

Fraction I and the contents of the trap were distilled at atmospheric pressure, and yielded 31.0 g of phenyl vinyl ether. Redistillation of Fraction II yielded:

1) 2.0 g (7.0% on the amount of the ether taken) of phenol, b. p. 68-70° at 3 mm, m.p. 41°.

2) 0.4 g (0.8% on the amount of the ether taken) of 2-methyl-3-phenyloxazolidine (VI), m.p. 58-59°.

Fraction III was treated with gasoline (b.p. 50-100°). The gasoline-insoluble part of the fraction (36.2 g) was found to be 2-anilinoethanol. Distillation of the gasoline solution yielded 0.4 g of acetaldehyde diphenyl acetal $CH_3CH(OC_6H_5)_2$: b.p. 135-136° (3 mm) and n_D^{20} 1.5590. The literature [16] gives: b.p. 146-148° (37 mm); n_D^{20} 1.5540; d_4^{20} 1.0808.

SUMMARY

1. The vinylation reaction of 2-anilinoethanol has been studied.

2. The vinyl and ethyl ethers of 2-anilinoethanol have been prepared and characterized.

3. Some of the reactions of the vinyl ether of 2-anilinoethanol have been investigated.

4. It has been found that, unlike other vinyl ethers of ethanolamines, the vinyl ether of 2-anilinoethanol undergoes a series of changes in presence of traces of concentrated hydrochloric acid with formation of 2-methyl-3-phenyloxazolidine, 2-anilinoethanol, and the compound $C_{12}H_{15}ON$.

5. It has been shown that alkyl (or aryl) 2-anilinoethyl acetals, like ethylene glycol and glycerol acetals, are readily converted into cyclic acetals under the conditions of the synthesis.

Received December 23, 1953

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

LITERATURE CITED

[1] M. F. Shostakovsky, I. A. Chekulaeva, and N. A. Gershtein, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1951, No. 3, 328.

[2] M. F. Shostakovsky and I. A. Chekulaeva, Bull. Acad. Sci. USSR. Div. Chem. Sci., 1953, No. 2, 368.*

[3] M. F. Shostakovsky and I. A. Chekulaeva, Bull. Acad. Sci. USSR. Div. Chem. Sci., 1954, No. 6, 1111.

[4] A. E. Favorsky and M. F. Shostakovsky, Authors' Certificate 59308 (1941); J. Gen. Chem., 13, 1 (1943).

[5] J. W. Copenhaver, M. H. Bigelow, Acetylene and carbon monoxide chemistry, New York, 1949.

[6] L. Knorr, H. Matthes, Ber. 34, 3484 (1901).

[7] M. F. Shostakovsky and E. P. Gracheva, J. Gen. Chem., 19, 1250 (1949).**

[8] M. F. Shostakovsky and P. V. Tyupaev, Syntheses of Organic Compounds, II, Acad. Sci. USSR Press, 1952 p. 39.

[9] M. F. Shostakovsky, N. A. Gershtein, and Z. S. Volkova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1952, No. 4, 671;*** 1953, No. 1, 100****

[10] M. F. Shostakovsky, V. V. Zhebrovsky, and M. A. Medelyanovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 1, 166.*****

[11] Yu. K. Yuryev, K. Yu. Novitsky, and L. G. Liberov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1951, No. 3, 317.

---

* See Consultants Bureau Translation, p. 335.
** " " " " p. 1243.
*** " " " " p. 617.
**** " " " " p. 89.
***** " " " " p. 137.

[13] M. F. Shostakovsky, E. N. Prilezhaeva, J. Gen. Chem., 17, 1132 (1947).

[14] L. C. Swallen, C. E. Boord, J. Am. Chem. Soc., 52, 651, (1930); C 1930, I, 3426.

[15] M. F. Shostakovsky, N. A. Gershtein, J. Gen. Chem., 16, 937 (1946).

[16] M. F. Shostakovsky, A. V. Bogdanova, J. Gen. Chem., 20, 1326 (1950)*.

---

* See Consultants Bureau Translation, p. 1379.

BLANK
PAGE

SYNTHESIS OF SULFUR COMPOUNDS

BY THE AID OF VINYL ETHERS AND ACETYLENE

COMMUNICATION 11. ION-CATALYZED REACTIONS OF ETHYL VINYL SULFIDE

M. F. Shostakovsky, E. N. Prilezhaeva, and N. I. Uvarova

Alkyl vinyl sulfides of general formula $RSCH{=}CH_2$, where R is a substituted or unsubstituted alkyl group of any structure and may contain various functional groups, are new compounds that have been little studied. We have previously made a comparative study of some properties of ethyl vinyl sulfide and ethyl vinyl ether, and have shown that, although both of these compounds can undergo free-radical reactions, the tendency to react in this way is more pronounced in ethyl vinyl sulfide [1,2,3]. This view is confirmed by an examination of the polymerization of ethyl vinyl sulfide and its addition reactions with thiols and hydrogen sulfide [3,4]. It is shown in the present paper that reaction of ethyl vinyl sulfide with alcohols, water, and hydrogen halides in presence of ionic catalysts always occurs in accordance with Markovnikovs rule.

The hydrolysis of ethyl vinyl sulfide was carried out in two ways: by means of a weakly acid solution of $NH_2OH \cdot HCl$, i.e., under the conditions used in the quantitative determination of vinyl ethers [5]; and by means of a solution of hydrochloric acid in a mixture of water and dioxane, acetaldehyde being determined in the hydrolyzate by the hydroxylamine method.

It was found that the hydrolysis of ethyl vinyl sulfide by means of a weakly acid solution of hydroxylamine hydrochloride (Equations 1, 2, and 3) requires much more severe conditions (longer time, higher temperature) than those required for ethyl vinyl ether (Table 1). For example, in two hours (the usual time for the quantitative hydrolysis of alkyl vinyl ethers) only 7-10 % of the ethyl vinyl sulfide reacts.

$$CH_2{=}CH-SC_2H_5 + H_2O \xrightarrow{H^{\cdot}} CH_3-CHO + C_2H_5SH; \qquad (1)$$

$$CH_3-CHO + NH_2OH \cdot HCl \longrightarrow CH_3CHNOH + HCl; \qquad (2)$$

$$CH_2{=}CHSC_2H_5 + H_2O + NH_2OH \cdot HCl \longrightarrow CH_3CHNOH + C_2H_5SH + HCl. \qquad (3)$$

It is easier to attain complete hydrolysis by the second method, but, in presence of HCl, half of the acetaldehyde formed in accordance with Equation 4 then reacts with the thiol that is also formed and yields acetaldehyde diethyl mercaptal (Equation 5). It might be supposed, therefore, that the overall reaction would be as indicated in Equation 6.

$$2CH_2{=}CHSC_2H_5 + 2H_2O \xrightarrow{H^{\cdot}} 2CH_3CHO + 2C_2H_5SH; \qquad (4)$$

$$CH_3CHO + 2C_2H_5SH \xrightarrow{H^{\cdot}} CH_3CH(SC_2H_5)_2 + H_2O; \qquad (5)$$

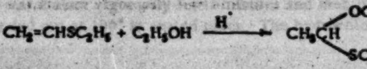
$$2CH_2{=}CHSC_2H_5 + H_2O \xrightarrow{H^{\cdot}} CH_3CHO + CH_3CH(SC_2H_5)_2. \qquad (6)$$

Under the conditions of the reaction, however, the formation of the mercaptal is a reversible process, as will be shown in the experimental part of this paper.

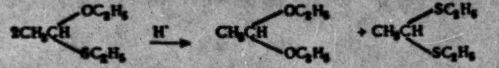
$$CH_3CH(SC_2H_5)_2 + 2H_2O \rightleftharpoons CH_3CHO + 2C_2H_5SH \qquad (7)$$

Owing to the superposition of all these reactions, the amount of acetaldehyde in the reaction mixture never corresponds exactly either to Equation 4 or to the overall Equation 6 (see Table 2), so that hydrolysis followed by titration of free acetaldehyde cannot be used for the quantitative determination of ethyl vinyl sulfide.

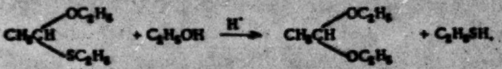
The reaction of ethyl vinyl sulfide with ethanol was studied. It was found that this reaction is very slow. The resulting monothioacetal is unstable and has a still greater tendency to undergo disproportionation and transetherification reactions (Equation 9 and 10) than the mixed acetals investigated by Shostakovsky and coworkers [1]:



$$CH_2{=}CHSC_2H_5 + C_2H_5OH \xrightarrow{H^{\cdot}} CH_3CH\begin{cases} OC_2H_5 \\ SC_2H_5 \end{cases} \qquad (8)$$



$$2CH_3CH\begin{matrix}OC_2H_5\\SC_2H_5\end{matrix} \xrightarrow{H^+} CH_3CH\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix} + CH_3CH\begin{matrix}SC_2H_5\\SC_2H_5\end{matrix} \qquad (9)$$



$$CH_3CH\begin{matrix}OC_2H_5\\SC_2H_5\end{matrix} + C_2H_5OH \xrightarrow{H^+} CH_3CH\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix} + C_2H_5SH. \qquad (10)$$

The addition of ethanol to ethyl vinyl sulfide is therefore accompanied by side reactions, so that only a low yield of the primary product is obtained. This behavior is very different from that of vinyl ethers in their reactions with alcohols, which proceed almost quantitatively.

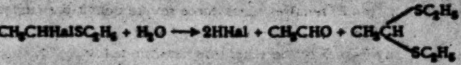
We studied also the reactions of ethyl vinyl sulfide with hydrogen chloride and hydrogen bromide. These reactions were carried out under the conditions already described for the hydrohalogenation of vinyl ethers [1,6]. In both cases high yields of the corresponding ethyl 1-haloethyl sulfides were obtained, i.e., addition of hydrogen halide is in accord with Markovnikov's rule. The hydrohalogenation of ethyl vinyl sulfide differs from that of ethyl vinyl ether in that no marked rise in temperature is to be observed.

$$CH_2{=}CHSC_2H_5 + HCl \longrightarrow CH_3CHClSC_2H_5; \qquad (11)$$

$$CH_2{=}CHSC_2H_5 + HBr \longrightarrow CH_3CHBrSC_2H_5. \qquad (12)$$

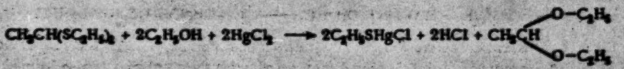
We did not succeed in effecting the addition of hydrogen bromide to ethyl vinyl sulfide in the direction contrary to that required by Markovnikov's rule by carrying out the reaction in an inert solvent in presence of an active free-radical initiator, 2,2'-azobis[2-methylpropionitrile]. Under these conditions a good yield was obtained of the same product as before, 1-bromoethyl ethyl sulfide. Hence, statements in the literature [7] concerning the readiness with which "anomalous" addition reactions occur between hydrogen bromide and vinyl sulfides are inaccurate.

The structures of the synthesized ethyl 1-haloethyl sulfides were proved by a hydrolysis method based on the fact that they are rapidly and quantitatively decomposed by cold water. The great tendency for ethyl 1-haloethyl sulfides to undergo hydrolysis shows how extremely mobile the halogen atoms are in these compounds [8]:



$$2CH_3CHHalSC_2H_5 + H_2O \longrightarrow 2HHal + CH_3CHO + CH_3CH\begin{matrix}SC_2H_5\\SC_2H_5\end{matrix} \qquad (13)$$

All of the components of the hydrolyzate can be determined quantitatively: hydrohalic acid, alkalimetrically; acetaldehyde by the hydroxylamine method; and the mercaptal by alkali titration of a solution obtained by addition of excess of ethanolic mercuric chloride (the mercuric chloride method, Equation 14):



$$CH_3CH(SC_2H_5)_2 + 2C_2H_5OH + 2HgCl_2 \longrightarrow 2C_2H_5SHgCl + 2HCl + CH_3CH\begin{matrix}O{-}C_2H_5\\O{-}C_2H_5\end{matrix} \qquad (14)$$

It has been shown already that the halogen of α-halo ethers can be determined quantitatively by titration of their hydrolyzates [6]. The titration of the hydrolyzate forms a method of analysis also for alkyl 1-haloethyl sulfides, since by this means the sulfur and halogen contents of these substances can be determined quantitatively.

1-Chloroethyl ethyl sulfide is more stable to storage than 1-bromoethyl ethyl sulfide, so that the same order is observed here as was observed for α-halo ethers [9]. Dilution with diethyl ether is as effective for the stabilization of these substances as it is for that of their oxygen analogs [9].

It follows from the above discussion that the hydrohalogenation of ethyl vinyl sulfide differs comparatively little from the corresponding reaction of ethyl vinyl ether.

Hence, the ion-catalyzed reactions of ethyl vinyl sulfide with water, alcohol, and hydrogen halides have their specific features, but their general character points to a close analogy between this substance and alkyl vinyl ethers.

EXPERIMENTAL

1. Study of the Conditions Required for the Hydrolysis of Ethyl Vinyl Sulfide

a) Hydrolysis of Ethyl Vinyl Sulfide with 0.5 N $NH_2OH \cdot HCl$ (Equations 1, 2, and 3). The hydrolysis was carried out under conditions similar to those described for alkyl vinyl ethers [5]. A weighed amount (0.15-0.25 g) of ethyl vinyl sulfide was introduced into a flask having a ground-in stopper and containing 10 ml of 0.5 N $NH_2OH \cdot HCl$. The mixture was shaken vigorously for 15 minutes and then maintained at 20-30° for 2-24 hours. Other experiments were carried out at 100° in sealed tubes. The hydrochloric acid liberated was titrated with 0.5 N

TABLE 1

Hydrolysis of Ethyl Vinyl Sulfide with 0.5 N $NH_2OH \cdot HCl$

Expt. No.	Duration of heating, hrs.	Temperature, (°C)	x
1	2	30	4.1
	2	30	3.9
2	24	20 - 30	57.80
	24	20 - 30	67.4
3	0.5	100	72.60
	0.5	100	71.40

TABLE 2

Hydrolysis of Ethyl Vinyl Sulfide in Presence of Hydrochloric Acid

Expt. No.	Duration of heating, hrs.	Temperature (°C)	x
1	1	100	103.6
	1	100	102.1
2	4	100	112.0
	4	100	110.7
3	6	100	108.5
	6	100	108.0
4	11	100	148.2
	13	60	156.4

NaOH with Bromophenol Blue as indicator. As the reaction mixture had a strong odor of ethanethiol, the titration was carried out in a fume cupboard.

The calculation was carried out according to the formula $x = \frac{88.16(a-b)F \cdot 100}{2 \cdot 1000\,p}$ (see Equation 3) (x is the proportion of the ethyl vinyl sulfide that has been hydrolyzed (%); a is the volume (ml) of 0.5 N NaOH having a factor of F required in the titration; b is the acidity of 10 ml of the hydroxylamine solution (ml of the same caustic soda solution); and p is the weight of ethyl vinyl sulfide taken).

b) Hydrolysis of Ethyl Vinyl Sulfide with Hydrochloric Acid (Equations 4, 5, and 6). 1) A mixture of 5.24 g of ethyl vinyl sulfide, 10 ml of 5% HCl, 25 ml of dioxane, and 25 ml of water was heated in a sealed tube in a boiling water bath for six hours. The aqueous layer was separated from the mercaptal and transferred to a measuring flask. The mercaptal was washed out with ether, and the ether solution was washed several times with water and dried over sodium sulfate. Removal of ether and distillation of the residue yielded 3.4 g (76.0% yield according to Equation 6) of acetaldehyde diethyl mercaptal, b.p. 64-66° (6 mm) and n_D^{20} 1.5023, i.e. having constants close to those given in the literature [10].

Determination of free acetaldehyde in the aqueous solution by the hydroxylamine method gave a value of 0.99 g (75.8%).

2) Using similar conditions but smaller samples of the sulfide (0.3-1 g), we attempted to apply the method for the quantitative determination of ethyl vinyl sulfide. The percentage x of hydrolyzed ethyl vinyl sulfide was determined by titration of the free acetaldehyde in a aliquot of the hydrolyzate by the hydroxylamine method. The calculation was carried out in accordance with Equation 6 by the use of the following formula (in this case, 0.1 N NaOH was used):

$$x = \frac{2 \cdot 88.16\,(a-b)\,F \cdot 100}{10 \cdot 1000 \cdot p} \qquad \text{(see Equation 6).}$$

The results are given in Table 2.

It will be clear from Table 2 that after one hour the extent of hydrolysis is fairly close to that required by the overall Equation 6. When heating is more prolonged, the amount of free acetaldehyde increases greatly.

The experiment that we shall now describe shows that this effect is associated with the hydrolysis of the mercaptal that is formed in the first place (Equation 7). Acetaldehyde diethyl mercaptal (0.3368 g) was heated in a closed tube with a mixture of 4 ml of 5% HCl, 25 ml of water, and 25 ml of dioxane under the conditions of Experiment No. 4 (Table 2). The tube was then cooled, and its contents were transferred to a measuring flask. Determination of acetaldehyde by the hydroxylamine method showed that under these conditions hydrolysis of the diethyl mercaptal had occurred to the extent of 34-35%.

2. Investigation of the Conditions required for the Addition of Ethanol to Ethyl Vinyl Sulfide

a) Addition of Ethanol to Ethyl Vinyl Sulfide in presence of SO_2 (Equations 8, 9, and 10). Ethanol (4.6 g, i.e. 0.1 mole) was added to 6 g (0.07 mole) of ethyl vinyl sulfide contained in a three-necked flask fitted with stirrer and reflux condenser. The reaction mixture was cooled to −10°, and a slow current of SO_2 was passed through it for five minutes. The temperature of the reaction mixture then slowly rose to 24°. The mixture was stirred for 2 hours 30 minutes, and was then set aside overnight. On the next day the mixture was heated for five hours at 60°, and then fractionated. The following fractions were obtained:

Fraction I, in a cooled trap:	4.8 g
Fraction II, b.p. 71-74° (14 mm):	2.6 g
Resinous residue:	2.0 g

Fraction II was acetaldehyde diethyl mercaptal (50% yield). After refractionation it had the following constants: b.p. 67-68° (13mm); n_D^{20} 1.5025; d_4^{20} 0.9706; these are in accord with the data in the literature [10]. Values obtained by the mercuric chloride method (Equation 14) for the content of diethyl mercaptal were 98.1 and 97.6%.

The fraction collected in the trap was fractionated at ordinary pressure and yielded

Fraction I	B.p. 34-74°:	0.3 g:	n_D^{20} 1.4025	(odor of ethanethiol)
Fraction II	B.p. 74-78°:	3.5 g:	n_D^{20} 1.3815	
Fraction III	B.p. 78-80°:	0.3 g:	n_D^{20} 1.3840	
Resinous residue		0.4 g		

Fractions II and III were mixtures of acetaldehyde diethyl acetal and ethanol: this was shown by analysis of these fractions by the hydroxylamine method. The content of the diethyl acetal in these fractions was 45-47%.

Results on the addition of ethanol to ethyl vinyl sulfide in presence of SO_2 at different temperatures are given in Table 3.

TABLE 3

Addition of C_2H_5OH to $CH_2{=}CH-S-C_2H_5$ in presence of SO_2

Expt. No.	Molar ratio of ethyl vinyl sulfide and alcohol	Duration of heating (hours)	Temperature (°C)	Yield of the diethyl mercaptal (%)
1	1:1.5	6	60	50.0
2	1:1.5	24	20	46.3

b) Addition of C_2H_5OH to Ethyl Vinyl Sulfide in presence of HCl in Dioxane, Aqueous 30% HCl or $CH_3CHBrSC_2H_5$. A mixture of 5 g of ethyl vinyl sulfide and 2.6 g of ethanol was placed in a three-necked flask fitted with a stirrer, and 0.1 g of a solution of HCl in dioxane (25-27%) was added. No rise in temperature was observed. The reaction mixture was stirred for three hours and was then set aside overnight. It was then heated for 90 minutes at 55-60°. It was neutralized with potassium carbonate, and then fractionated, the following fractions being obtained:

Fraction I,	in a cooled trap:	3.5 g
Fraction II,	B.p. 25-65° (50 mm):	0.5 g
Fraction III,	B.p. 65-70° (50 mm):	1.3 g
Fraction IV,	B.p. 65-70° (12 mm):	1.1 g

Fractions I and II consisted of mixtures of alcohol, acetaldehyde diethyl acetal, and ethanethiol, for they had the same properties as the fractions obtained in this temperature range in the preceding experiment. Fraction IV was the diethyl mercaptal. Fraction III, boiling range 65-70° (50 mm), was united with several similar fractions from other experiments, and the combined fractions were fractionally distilled. The properties of the substance obtained were b.p. 66.5-67° (46 mm); n_D^{20} 1.4451; d_4^{20} 0.9038; found MR 39.55; calculated MR 39.52.

	Found %:	C 53.57; 53.84;	H 10.47; 10.47;	S 23.72; 23.62
$C_6H_{14}SO$.	Calculated %:	C 53.66;	H 10.51;	S 23.87

These constants coincide with those given in the literature [11, 12] for the monothioacetal. Titration by the mercuric chloride method showed that the fraction contained 98% of the monothioacetal.

The results for the addition of ethanol to ethyl vinyl sulfide in presence of hydrogen chloride in dioxane, of 30% aqueous HCl, and of $CH_3-CHBrSC_2H_5$ are summarized in Table 4 (5-10 g of the sulfide was taken).

c) Reaction of the Monothioacetal with Ethanol in presence of SO_2 (Equation 10). A slow current of SO_2 was passed for five minutes through a cooled (0°) mixture of 6.5 g (0.05 mole) of the monothioacetal and 4.6 g (0.1 mole) of ethanol. No rise in temperature was observed. The mixture was heated at 60-65° for 90 minutes. Two days later it was fractionated, and the following fractions were obtained:

TABLE 4

Addition of C_2H_5OH to $CH_2{=}CH-S-C_2H_5$ in presence of Hydrogen Chloride in Dioxane, 30% Aqueous HCl, or $CH_3CHBrSC_2H_5$

Expt. No.	Molar ratio of ethyl vinyl sulfide and alcohol	Catalyst (g)	Duration of heating (hours)	Temperature (°C)	Yield of monothioacetal (%)
1	1:1	0.1 g HCl in dioxane (~27%)	1.5	80	20.0
2	1:1.8	" "	48	18	12.0
3	1:1.2	0.1 g HCl (30% aqueous)	48	18	11.0
4	1:1.2	0.1 g $CH_3CHBrSC_2H_5$	48	18	10.5

Fraction I,	in cooled trap (42 mm):	4.4 g
Fraction II,	B.p. 20-60° (42 mm);	1.9 g
Fraction III,	B.p. 50-80° (42 mm);	2.6 g
Fraction IV,	B.p. 50-65° (12 mm);	1.0 g
Resinous residue:		1.0 g

Fractions I, II, and III were fractionated at ordinary pressure. They yielded:

Fraction I,	B.p. 30 - 44°;	0.2 g	
Fraction II,	B.p. 44 - 74°;	0.2 g	
Fraction III,	B.p. 74 - 80°;	5.4 g;	n_D^{20} 1.3702
Fraction IV,	B.p. 80 - 100°;	1.4 g;	n_D^{20} 1.3940
Resinous residue		1.5 g;	

Fraction I was ethanethiol. Acetaldehyde diethyl acetal was present in Fraction III to the extent of 32-33%, and in Fraction IV to the extent of 76-77%.

3. Hydrohalogenation of Ethyl Vinyl Sulfide

a) Addition of Hydrogen Chloride (Equation 11). Ethyl vinyl sulfide (9.3 g) was placed in a three-necked flask fitted with stirrer, condenser, and tube for passage of gas, and was cooled to −10°. A current of dry hydrogen chloride. When hydrogen chloride began to leave by the condenser, its passage was discontinued. Fractionation yielded:

Fraction I,	B.p. 36-46° (30 mm);	0.6 g
Fraction II,	B.p. 46-47° (30 mm);	10.6 g

Fraction II was 1-chloroethyl ethyl sulfide (80.9% yield). After refractionation its properties were b.p. 64-47° (30 mm); n_D^{20} 1.4705; d_4^{20} 1.012; found MR 33.44; calculated MR 33.50.

Found%*: Cl 28.41; 28.18; S 25.13; 25.10

C_4H_9ClS, Calculated %: Cl 28.45; S 25.74

The following constants are given in the literature for 1-chloroethyl ethyl sulfide: b.p. 42-45° (25 mm) [13] and b.p. 39° (24 mm) [8].

b) Reaction of 1-Chloroethyl Ethyl Sulfide with Water (Equation 13). A weighed amount of 1-chloroethyl ethyl sulfide was introduced into a measuring flask containing water. The contents of the flask were shaken, allowed to stand for 15 minutes, and brought to the mark with alcohol. Hydrogen chloride was determined alkalimetrically, acetaldehyde by the hydroxylamine method, and mercaptal by the mercuric chloride method. The results of the determinations in two parallel experiments are given in Table 5.

TABLE 5

Reaction of 1-Chloroethyl Ethyl Sulfide with Water

Expt. No.	Amount of 1-chloroethyl ethyl sulfide taken (g)	Yield (%)		
		HCl	acetaldehyde	mercaptal
1	1.2340	99.86	98.77	97.67
2	1.2427	99.06	99.36	97.57

---

* Determined by titration of the hydrolyzate (see Table 5).

1-Chloroethyl ethyl sulfide keeps satisfactorily in a flask having a ground-in stopper for 7-8 days; it then begins to resinify. When diluted with absolute ether, it can be preserved without change for several months.

c) Addition of Hydrogen Bromide (Equation 12) (Experiment No. 1). The addition of HBr was carried out under the same conditions as those used for the addition of HCl. From 8.5 g of ethyl vinyl sulfide, 16.5 g of crude 1-bromoethyl ethyl sulfide was obtained (the theoretical amount was 16.2 g). The excess of hydrogen bromide was removed with the aid of a water pump. Fractionation yielded 12.5 g a substance of b.p. 45-50° (7.5 mm) (residue in flask 2 g). The yield of 1-bromoethyl ethyl sulfide was 77.1%. After refractionation the product had the following constants: b.p. 39-41.5° (5 mm); n_D^{20} 1.5130; d_4^{20} 1.3677; found MR 37.18; calculated MR 36.47

Found* %: Br 46.69; 46.64; S 18.80; 18.70

C_4H_9BrS. Calculated %: Br 47.25; S 18.90

The substance fumed strongly in air, and it began to turn brown after the first day. When diluted with absolute ether it can be preserved without change for several months.

d) Addition of Hydrogen Bromide in a Pentane Medium in presence of 2,2'-Azobis[2-methylpropionitrile] (Experiment No. 2). A mixture of 3.4 g of ethyl vinyl sulfide, 14 g of pentane, and 0.05 g of 2,2'-azobis[2-methylpropionitrile] was prepared in an ampoule. Nitrogen was blown through the ampoule, first at room temperature, and then under cooling. Hydrogen bromide (3.5 g) was then condensed in the ampoule, which was then cooled in liquid nitrogen, evacuated for 20 minutes, and sealed. The ampoule was heated for two hours at 60-70°, and then set aside overnight. Fractionation yielded 5.2 g of a substance of b.p. 45-47° (7 mm); n_D^{20} 1.5130 (residue in flask 0.2 g). The yield was 79.6%.

e) Reaction of 1-Bromoethyl Ethyl Sulfide with Water (Equation 13). A weighed amount of 1-bromoethyl ethyl sulfide was shaken in a measuring flask with 10-15 ml of water for 15 minutes. The determination of the components of the hydrolyzate [HBr, CH_3CHO, and $CH_3CH(SC_2H_5)_2$] was carried out by the methods used for 1-chloroethyl ethyl sulfide. The results of the titrations of the bromo compounds obtained under different conditions are given in Table 6.

Addition of HBr to ethyl vinyl sulfide, both in presence of 2,2'-azobis[2-methylpropionitrile] (Experiment No. 2), and in its absence (Experiment No. 1), proceeds exclusively in the direction required by Markovnikov's rule.

TABLE 6

Reaction of 1-Bromoethyl Ethyl Sulfide with Water

Expt. No.	Amount of 1-bromoethyl ethyl sulfide taken (g)	Yield (%)		
		HBr	acetaldehyde	mercaptal
1	1.1436	98.8	99.6	99.6
2	1.6236	98.75	99.3	98.8

SUMMARY

1. The ion-catalyzed reactions of ethyl vinyl sulfide with water, with ethanol, with hydrogen chloride, and with hydrogen bromide have been studied, and it has been shown that addition occurs in the direction required by Markovnikov's rule, i.e. as in the similar reactions of vinyl ethers.

2. The conditions have been determined for the hydrolysis of ethyl vinyl sulfide. It has been shown that its hydrolysis by a weakly acid solution of $NH_2OH \cdot HCl$ is much slower than that of ethyl vinyl ether. Ethyl vinyl sulfide undergoes hydrolytic decomposition when treated with a solution of HCl in a mixture of water and dioxane, acetaldehyde and acetaldehyde diethyl mercaptal being obtained.

3. A study has been made of the conditions required for the addition of alcohol to ethyl vinyl sulfide with formation of a monothioacetal. Some of the properties of the monothioacetal have been studied.

4. The conditions required for the hydrohalogenation of ethyl vinyl sulfide have been determined. The addition of hydrogen chloride and of hydrogen bromide has been effected with formation of the ethyl 1-haloethyl sulfides in about 80% yield. It has been shown that ethyl 1-haloethyl sulfides are hydrolyzed by water in the cold, with quantitative formation of hydrogen halide, acetaldehyde, and acetaldehyde diethyl mercaptal.

Received November 14, 1953

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

---

* Determined by titration of the hydrolyzate (see Table 6).

LITERATURE CITED

[1] M. F. Shostakovsky, Vinyl Ethers, Acad. Sci. USSR Press, Moscow, 1952, pp. 212-256.

[2] M. F. Shostakovsky, E. N. Prilezhaeva, and E. S. Shapiro, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1951, No. 4, 438.

[3] M. F. Shostakovsky, E. N. Prilezhaeva, and N. I. Uvarova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 3, 526. *

[4] E. N. Prilezhaeva and M. F. Shostakovsky, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 3, 517. **

[5] M. F. Shostakovsky and E. N. Prilezhaeva, J. Gen. Chem., 17, 1129 (1947); M. F. Shostakovsky, E. N. Prilezhaeva, and N. I. Uvarova, J. Anal. Chem., 6, 348 (1951).

[6] M. F. Shostakovsky and A. V. Bogdanova, J. Gen. Chem., 17, 565 (1947).

[7] C. Whither, E. E. Reid, J. Am. Chem. Soc. 43, 636-638 (1921).

[8] H. Böhme, H. Fischer, R. Frank, Ann. 563, 354 (1949).

[9] M. F. Shostakovsky and A. V. Bogdanova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 1, 162. ***

[10] E. Fromm, Ann. 253, 140 (1889).

[11] M. F. Shostakovsky, E. N. Prilezhaeva, and E. S. Shapiro, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, No. 2, 357. ****

[12] F. F. Kipnis, H. Soloway, J. Ornfelt, J. Am. Chem. Soc. 73, 1783 (1951).

[13] L. Ramberg, B. Bächlund, Arkiv f. Kemi, Mineralogi, Geologi 13, No. 27 (1940).

---

* See Consultants Bureau Translation, p. 447.

** " " " " p. 439.

*** " " " " p. 133.

**** " " " " p. 325.

MACROMOLECULAR COMPOUNDS

COMMUNICATION 69. DEPENDENCE OF THE PROPERTIES OF POLYAMIDES ON THE EXTENT OF INTERMOLECULAR HYDROGEN BONDING

V. V. Korshak and T. M. Frunze

The great mechanical strength and high melting points of polyamides have been explained by some authors as due to the occurrence of hydrogen bonding between the macromolecules [1, 2, 3]. This view finds support in the fact that the molecular cohesion forces are greatly different for methylene and for amide groups. Thus, for the methylene group the molecular cohesion energy is 1780 cal/mole, and for the amide group it is 16,200 cal/mole [4]. The proportion of amide linkages will therefore play an important part in determining the properties under consideration. Thus, when the properties of polyesters and polyamides derived from adipic acid are compared, the great differences between them are readily seen.

Polyhexamethylene adipate $[-CO-(CH_2)_4-CO-O-(CH_2)_6-O-]_x$ melts at 56° [5], but polyhexamethyleneadipamide $[-CO-(CH_2)_4-CO-NH-(CH_2)_6-NH-]_x$ melts at 250° [6]. Since the melting point provides a measure of the extent of the interaction between macromolecular chains, these values for the melting points indicate the great difference between these compounds. It is clear that the extent of the interaction between the chains will be associated with the proportion of polar amide groups present, and this interaction will be reflected in the value of the melting point. There are data in the literature that illustrate this dependence, and these include the following (Table 1), which relate to polyamides formed by adipic acid with various diamines.

TABLE 1

Polyamide	Formula	Number of methylene groups in the diamine	M.p. (°C)
Polydimethyleneadipamide	$-CO(CH_2)_4CONH(CH_2)_2NH-$	2	308
Polytetramethyleneadipamide	$-CO(CH_2)_4CONH(CH_2)_4NH-$	4	278
Polyhexamethyleneadipamide	$-CO(CH_2)_4CONH(CH_2)_6NH-$	6	250
Polyoctamethyleneadipamide	$-CO(CH_2)_4CONH(CH_2)_8NH-$	8	235
Polydecamethyleneadipamide	$-CO(CH_2)_4CONH(CH_2)_{10}NH-$	10	230

A second way in which the proportion of hydrogen bonds may be reduced consists in the creation of conditions that inhibit hydrogen-bond formation between amide groups, and this may be effected either by replacement of the amide hydrogen or by variation in the distances between amide linkages. Such variation occurs in mixed polyamides formed by reaction between several diamines and dicarboxylic acids.

The present investigation was undertaken to determine the effect of variation in the extent of hydrogen bonding on the properties of the polyamide.

EXPERIMENTAL PROCEDURE

We prepared mixed polyamides by reaction of 1,6-hexanediamine with a pair of dicarboxylic acids selected from adipic, suberic, azelaic, and sebacic acids. The choice of acids was determined by the need for obtaining polyamides in which the distances between the amide groups would vary within sufficiently wide limits. Among the polyamides so obtained, that obtained by the polycondensation of 1,6-hexanediamine with a mixture of adipic and sebacic acids has been described by Catlin, Czerwin, and Willey [8], and also by Stastny [9]. We may mention here that the melting point curve that we obtained for this system is in agreement with that described in the literature.

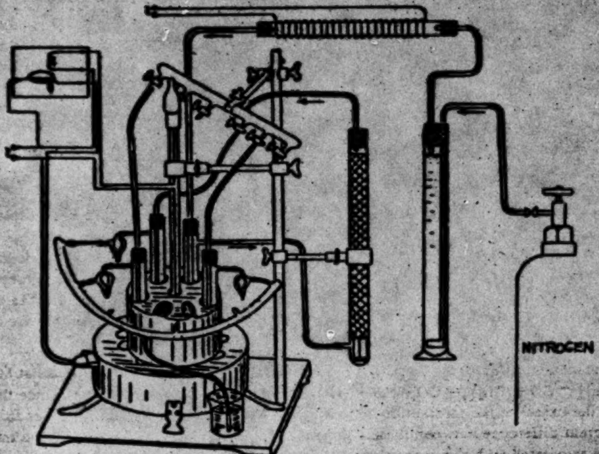


Fig. 1.

Polycondensation was brought about by heating a mixture of the starting materials in a current of pure nitrogen, the temperature being gradually raised from 170-200° to 250-260°, depending on the properties of the starting materials. The heating was carried out in the apparatus shown in Fig. 1. The original substances were placed in test tubes having side arms, which were all connected to one common tube having a single outlet tube, which dipped into water. The nitrogen was carefully purified from oxygen, being passed through an alkaline solution of pyrogallol and a silica tube filled with copper-covered silica gel heated to 450°. The nitrogen was then dried over calcium chloride and phosphoric anhydride and exhaustively purified from oxygen by passage through molten polyamide at 250°. The test tubes were heated in an alloy bath, the temperature being controlled with the aid of an electronic relay.

The melting points of the resulting polyamides were determined by heating small pieces in test tubes under a layer of molten paraffin wax. The test tubes were heated in a glycerol bath, and the rate of rise in temperature was 1-2° per minute. The value obtained for the melting point depends greatly on the rate at which the bath is heated. When heating is rapid, the melting point is considerably depressed, the difference sometimes amounting to 10°. Most mixed polyamides have a very much extended melting range. The substance first softens, then begins to become deformed under external influences, and finally melts. The temperature range from softening to melting varies, but is generally about 10°. The results are shown in Table 2. In addition to the melting points, the solubilities of the polymers in alcohol and in an alcohol-chloroform mixture were determined.

DISCUSSION OF RESULTS

The variation of melting point with composition is shown for the binary systems SubH– AdH, AzH– AdH, SebH – AdH in Fig. 2, and for the system AzH - SebH in Fig. 3*.

As will be seen from Figures 2 and 3, variation in the composition of the polymers results in variation of their melting points and of all of their other properties. Also, a close relationship is to be observed between such properties as melting point and solubility. The melting point falls and passes through a minimum, which corresponds in most cases to a product in which the mole fraction of the substance containing the dicarboxylic acid with the

---

* The products obtained from the salt SucH differed greatly in their properties from the remaining substances. It is probable that this resulted from differences in the course taken by the reaction. We propose to investigate the causes of this difference.

TABLE 2

Melting Points of the Investigated Binary Systems, °C

Molar ratio of starting substances **	Starting substances*				
	SucH/AdH	SubH/AdH	AzH/AdH	SebH/AdH	AzH/SebH
1.0/0.0	210 - 212	225 - 227	205 - 208	210 - 212	205 - 208
0.8/0.2	200 - 205	210 - 213	190 - 195	190 - 195	195 - 198
0.6/0.4	200 - 207	197 - 203	178 - 180	185 - 186	180 - 185
0.5/0.5	–	–	185 - 190	190 - 195	178 - 180
0.4/0.6	210 - 215	210 - 215	205 - 208	190 - 197	170 - 175
0.2/0.8	232 - 239	230 - 237	220 - 230	220 - 227	190 - 195
0.0/1.0	250 - 252	250 - 252	250 - 252	250 - 252	210 - 212

---

* The abreviations used are as follows: Suc - succinic acid; Sub - suberic acid; Az - azelaic acid; Seb - sebacic acid; Ad - adipic acid; H - 1,6-hexanediamine.

** In these ratios the numerator and denominator correspond to the numerator and denominator respectively of the "fraction" at the top of the column (under "Starting substances").

longer chain is 0.6; i.e. to a content of about 60% by weight of this component.

It should be noted that the position of the minimum is the lowest, the greater the length of the dicarboxylic acid molecule from which the original salt is derived. In the system SubH – AdH, for example, the maximum depression in the melting point is 53°, whereas in the system SebH – AdH it is 65°. It follows that sebacic acid, which has ten carbon atoms in its molecule, has a greater effect than suberic acid, which has only eight carbon atoms.

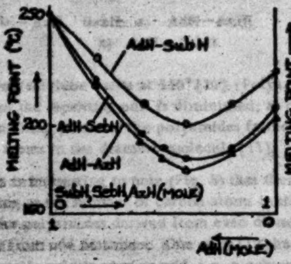


Fig. 2. o) AdH – SubH; ●) AdH – SebH;
Δ) AdH – AzH

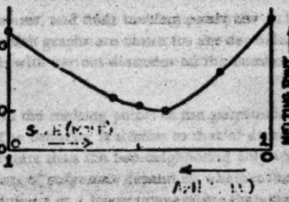


Fig. 3.

In the case of azelaic acid, there is a departure from this rule, for, although it has nine carbon atoms in its molecule (i.e. fewer than sebacic acid), it produces a greater melting point depression in the binary system AdH – AzH than sebacic acid does in the system AdH – SebH. In this first system the minimum melting point is 178°, and in the second 185°. This result evidently arises from the fact that azelaic acid is an "odd" acid, which cannot so readily form hydrogen bonds in the reaction product; we shall consider this matter in greater detail below. In the system SebH – AzH, although we here find the product with the lowest absolute value of melting point (170°), the relative fall in melting point compared with the melting points of the single original salts is only about 40°, i.e. less than in the other systems that we have studied.

All of the products were found to have very low sulubility in organic solvents, with the exception of cresol, in which they are readily soluble. They are readily soluble also in acids (sulfuric, hydrochloric, formic), in dimethylformamide, and in aqueous phenol, i.e. in the solvents in which the polyamides obtained from single 1,6-hexanediamine salts are readily soluble. Solvents may be placed in the following series of reducing solvent power for the system SebH – AzH: cresol, isopropyl alcohol, a mixture of ethanol and chloroform, methanol, ethanol, methyl cellosolve, ethyl cellosolve.

Fig. 4 shows the variation of solubility in a mixture of ethanol and chloroform with composition.

It will we seen from Fig. 4 that the solubility is the greater, the lower the melting point. Thus, the products obtained from the systems we have investigated can be placed in the following series of diminishing solubility: SebH – AzH, AzH – AdH, SebH – AdH, SubH – AdH. The solubilities of the products belonging to the last system are so low that they could not be shown on the graph.

Both the melting points and the solubilities of crystalline polymers are expressions of the interactions between the chains, i.e. of the forces binding the separate macromolecules of the polymer together in the particular sample of the macromolecular compound. The higher the melting point and the lower the solubility of the given polymer, the greater the forces binding the separate molecules to one another; conversely, the lower the melting point and the higher the solubility of the substance, the smaller the forces acting between the separate molecules. Since melting and dissolution are processes in which the crystal lattice of the polymer is disrupted, the readiness with which they occur is related to the strength of the polymer.

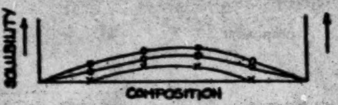


Fig. 4. o)– AzH SebH; •) AdH – AzH;
x) AcH SebH

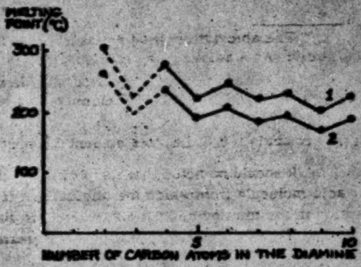


Fig. 5. 1) Polyamides of adipic acid; 2) polyamides of sebacic acid

Polyethylene melts at 110° [10]. Polyamides melt at higher temperatures, and their melting points rise as the length of the repeating unit is diminished, as can be seen from Fig. 5, in which graphs are shown for the dependence of the melting points of the polyamides formed by adipic and sebacic acids with various diamines on the number of carbon atoms in the diamine molecule [11].

It is interesting to note (Fig. 5) that there is a periodic rise and fall in the melting points of the polyamides according as the number of carbon atoms in the diamine is even or odd. The behavior is similar to that of dicarboxylic acids, for polyamides derived from even diamines melt at a higher temperature than the two neighboring polyamides derived from odd diamines. One of us [12] has shown that the melting points of polyesters depend on whether the dicarboxylic acid is even or odd, i.e. a polyester derived from an odd acid melts at a lower temperature than the two neighboring polyesters derived from even acids [13]. Hence, the odd-even effect plays the same part in the diamine series as in the dicarboxylic acid series.

We may conclude, therefore, that the high melting points of polyamides, as compared with polyethylene, are associated with the presence of amide linkages in their molecules. If we actually compare the melting points of the polyamides with the proportions of amide linkages expressed as a percentage of the number of methylene groups in the polyamide chain, we obtained the results given in Table 3.

The absence of data on the melting points of polyamides derived from other dicarboxylic acids prevented us from verifying this relationship more extensively.

The results given in Table 3 relate to polyamides derived from dicarboxylic acids having even numbers of carbon atoms in their molecules, for it was not possible to make use of data relating to polyamides derived from odd dicarboxylic acids owing to the odd-even effect, which would distort the results appreciably. When the data of Table 3 are expressed in the form of a graph in order to show the form of the dependence of melting point on the percentage content of amide linkages in the macromolecular chain, it is found that all of the points fall on a straight line (Fig. 6).

When this straight line is continued, as indicated in Fig. 6 by the broken line, it meets the ordinate axis at 110°, the melting point of polyethylene. There is therefore a linear relationship between the content of amide linkages in the polymer chain and the melting point. Polyethylene, of course, has a zero content of amide linkages,

TABLE 3

Dependence of the Melting Points of Polyhexamethyleneamides on their Percentage Contents of Amide Groupings

Name of polyamide and formula of repeating unit	Number of methylene groups in			Proportion of amide groupings (%)	M.p. of the polyamide (°C)
	the diamine	the acid	the repeating unit of the polyamide		
Polyhexamethyleneadipamide $-NH(CH_2)_6NHCO(CH_2)_4CO-$	6	4	10	20.0	250
Polyhexamethylenesuberamide $-NH(CH_2)_6NHCO(CH_2)_6CO-$	6	6	12	16.6	225
Polyhexamethylenesebacamide $-NH(CH_2)_6NHCO(CH_2)_8CO-$	6	8	14	14.3	210

and we may conclude that the melting point of a polyamide cannot be less than that of polyethylene. The presence of amide linkages results in a rise in melting point that is directly proportional to the proportion of these linkages. It must be remembered, of course, that this conclusion is valid only for polyamides derived from aliphatic dicarboxylic acids and aliphatic diamines having a straight chain not containing any substituents, as the relationship changes considerably for compounds of other types.

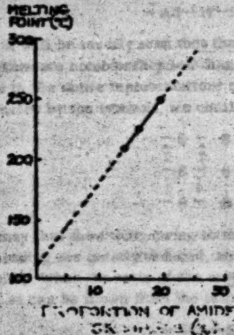


Fig. 6

The presence of amide groupings in the polyamide molecule makes hydrogen bonding possible, and this is responsible for all of the properties attributable to the presence of amide linkages in the molecule. The most important of these are the mechanical properties, the melting point, and the solubility. They are all manifestations of the magnitude of the forces binding the separate molecules together in the mass of the polymer, and the study of them is therefore very important for the complete characterization of the polymer.

For the formation of hydrogen bonds the distribution of amide groupings must be such that the distances between amide groups in neighboring molecules do not exceed 2.7 A, so that it is to be expected that the structure of the polymer chain can greatly affect the ease with which these bonds can arise. Polyamides derived from even and odd amino acids, and also from even and odd diamines and dicarboxylic acids, vary greatly in their melting points. This can be explained simply by the spatial disposition of the amide linkages and the resulting variation in the possibility for the formation of hydrogen bonds [14]. Polyamides derived from odd dicarboxylic acids therefore have lower melting points than those derived from even dicarboxylic acids. For the polyamides formed from mixtures of several dicarboxylic acids, the possibilities for hydrogen-bond formation may vary over a wide range on account of purely spatial factors.

As the proportions of the various units of the polyamide chain are varied, owing to variation in the proportions of the starting materials, the polymer will be found to contain varying proportions of units that differ in their lengths. The distribution of these units in the macromolecular chain must be fairly uniform, according to the results of previous investigations. Thus, one of us, in conjunction with Rafikov [15], Zamyatina [16], Golubev [17], Chelnokova [18], Vinogradova [19], and others, has shown that in various polycondensation reactions of dicarboxylic acids with diamines, glycols, amino alcohols, and other compounds (which occur at high temperature in presence of catalytically active substances, among which are the starting compounds themselves [20]), vigorous exchange reactions occur between the polymer molecules, starting substances, and low-molecular-weight reaction products under the conditions of the process [21]. As a result of these exchange reactions, units of different structure distribute themselves among the various polymer molecules in accordance with thermodynamic probability, which is determined by the number of units of different structure and the size of the polymer molecules [22].

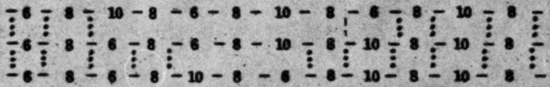
One of us, in conjunction with Chelnokova and Distler [23], carried out the polycondensation of 2-aminoethanol with sebacic acid and obtained a polyamidoester of the same structure as that obtained by the polycondensation of N,N'-bis(2-hydroxyethyl) sebacamide with sebacic acid. This result shows that, owing to the occurrence of exchange reactions during the polycondensation process, a redistribution of the individual units occurs; these units combine with one another in an unrestrained manner and in the order corresponding to the statistical probability of their distribution under the given conditions.

These results give us reason to suppose that polycondensation products present quite a different picture from that presented by copolymers obtained from vinyl monomers, for which convincing proof has been presented both of the nonuniform distribution of monomer residues among the polymer molecules and of their nonuniform distribution along the length of a given macromolecule [24, 25]. We may therefore assume that the polyamides that we have synthesized have molecules of identical structure containing like proportions of the residues of the starting substances distributed more or less uniformly along the length of the macromolecular chain.

These considerations enable us to make a more simple approach to the examination of the possibilities of hydrogen-bond formation between molecules of mixed polyamides. If there were no hindrances to the formation of hydrogen bonds between amide groupings in mixed polyamides, we should expect a smooth variation in melting point within the range of the melting points of the polyamides obtained from the single components. In actual fact, a considerable fall in melting point is observed, and the minimum lies at a mole fraction of 0.6 of the component containing the acid having the longer molecule. The obvious cause for this is the creation of obstacles to the participation of a fraction of the amide groupings in hydrogen bonding. If we examine the structure of the chain of a mixed polyamide, taking the product obtained from the salts SebH and AdH as an example, we may imagine the following distributions of residues in the macromolecule chain for the product containing these salts in the ratio 1:1 :

− Ad − H − Seb − H − Ad − H − Seb − H − Ad − H − Seb − H −
− Ad − H − Ad − H − Ad − H − Seb − H − Seb − H − Seb − H −
− Ad − H − Ad − H − Seb − H − Ad − H − Seb − H − Seb − H −

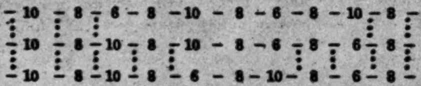
and so on. It will be readily seen that the possibilities for the formation of hydrogen bonds in molecules having this sort of structure are considerably less than in those of polyamides derived from a single component. If we replace the symbols in the above representations of the structure by the numbers of carbon atoms in the main chains of the residues denoted by the symbols, we obtain the following picture (the dotted lines indicate hydrogen bonds):



We may thus show that, owing to the variation in length of the individual components, the opportunities for hydrogen bonding are greatly reduced, and the reduction in the number of such bonds leads to an appreciable fall in melting point. When the ratio of the original salts is 2:3, the opportunities for the formation of hydrogen bonds become even rarer, as can be shown from the same sort of diagrammatic representation:

− Seb − H − Ad − H − Seb − H − Ad − H − Seb − H −
− Seb − H − Seb − H − Seb − H − Ad − H − Ad − H −
− Seb − H − Seb − H − Ad − H − Seb − H − Ad − H −

or, by the use of figures indicating the numbers of atoms in the units:



It will be readily seen that in this case the number of hydrogen bonds will be still less than in the previous case, both as a result of the greater number of methylene groups in sebacic acid, which predominates, and also as a result of hindrances of a purely spatial kind to their formation.

These diagrams are only illustrative and cannot be used for the calculation of the proportion of hydrogen bonds. For this purpose we may make use of the graph given in Fig. 6. The points corresponding to the melting points for 1:1 and 2:2 ratios in the system SebH − AdH are 190° and 185°, and have abscissas corresponding to proportions of hydrogen bonds of 11% and 10%. Calculation shows that these polyamides have 16.6% and 16.1% of amide linkages respectively. It may therefore be concluded that, owing to the peculiar features in the structures of mixed polyamides, only 66.2% of the total possible number of hydrogen bonds are realized in the first polyamide, and only 62.1% in the second. The remaining amide groupings are unable to approach one another sufficiently closely for the formation of hydrogen bonds, and their presence, therefore, has no effect on the properties of the polyamide.

SUMMARY

1. A number of mixed polyamides have been investigated from the point of view of the effect of hydrogen bonds on the properties of polyamides, and it has been shown that owing to steric hindrance a considerable proportion

of the amide groupings cannot interact through hydrogen bonds, this fact being reflected in all of the physical properties of the polymer.

2. The properties of mixed polyamide systems have been studied, the substances investigated being products of the reaction of 1,6-hexanediamine with a mixture of two dicarboxylic acids, selected from adipic, succinic, suberic, azelaic, and sebacic acids.

3. It has been shown that for polyamides derived from a given dicarboxylic acid and various diamines, the melting point varies with the number of carbon atoms in the diamine in accordance with a zig-zag curve, the melting point being higher when the number is even than when it is odd.

4. It has been found that the melting points of polyamides derived from dicarboxylic acids having even numbers of carbon atoms in their molecules vary linearly with the number of amide groupings (i.e. hydrogen bonds).

5. A graphical method has been proposed for the determination of the extent of intermolecular hydrogen bonding in mixed polyamides.

Received December 12, 1953

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

LITERATURE CITED

[1] H. L. Huggins, J. Org. Chem. 1, 440 (1936).

[2] G. F. Zellhoefer, M. J. Copley, C. S. Marvel, J. Am. Chem. Soc. 60, 1357 (1938).

[3] W. O. Baker, C. S. Fuller, J. Am. Chem. Soc. 64, 2399 (1942).

[4] H. Mark, Prog. Phys. Sci., 32, 239 (1947); Am. J. Phys. 13, 907 (1945).

[5] V. V. Korshak and S. V. Vinogradova, Proc. Acad. Sci. USSR, 94, 61 (1954).

[6] V. V. Korshak and S. R. Rafikov, J. Gen. Chem., 14, 974 (1944).

[7] I. D. Coffman, G. J. Berchet, W. R. Peterson, E. W. Spanagel, J. Polymer Sci. 2, 306 (1947).

[8] W. E. Catlin, E. P. Czerwin, R. H. Willey, J. Polymer Sci. 2, 412 (1947).

[9] F. Stastny, Kunststoffe 40, 273 (1950).

[10] V. V. Korshak, Chemistry of Macromolecular Compounds, Acad. Sci. USSR Press, Moscow and Leningrad, 1950, p. 353.

[11] V. V. Korshak, Methods of Macromolecular Organic Chemistry, Part 1, General Methods for the Synthesis of Macromolecular Compounds, Acad. Sci. USSR Press, Moscow, 1953, p. 449.

[12] V. V. Korshak and S. V. Vinogradova, Proc. Acad. Sci. USSR, 89, 1017 (1953).

[13] V. V. Korshak and S. V. Vinogradova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, 1089.

[14] R. Hill, E. E. Walker, J. Polymer Sci. 3, 609 (1948).

[15] S. V. Rafikov, V. V. Korshak, and L. N. Pinkina, J. Gen Chem., 14, 1003 (1944).

[16] V. V. Korshak and V. A. Zamyatina, Proc. Acad. Sci. USSR, 59, 909 (1948).

[17] V. V. Korshak and V. V. Golubev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1946, No. 2, 185

[18] G. N. Chelnokova and V. V. Korshak, Collection of Papers on General Chemistry, 2, 1953, p. 1070.

[19] V. V. Korshak and S. V. Vinogradova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1952, 1109.*

[20] V. V. Korshak, Papers read at the Thirteenth International Congress of Theoretical and Applied Chemistry, Acad. Sci. USSR Press, Moscow, 1953, p. 267.

[21] V. V. Korshak, Prog. Chem., 21, 137 (1952).

[22] V. V. Korshak, S. R. Rafikov, and V. A. Zamyatina, in the Collection "Investigations on Macromolecular Compounds", Acad. Sci. USSR Press, Moscow and Leningrad, 1949, p. 3.

[23] V. V. Korshak, G. N. Chelnokova, and G. I. Distler, Proc. Acad. Sci. USSR, 82, 569 (1952).

[24] B. N. Rutovsky and A. M. Shur, in the Collection "Macromolecular Compounds", No. 6, State Chem. Press, Moscow, 1947, p. 1.

[25] S. N. Ushakov, S. P. Mitsengendler, and G. A. Shtraikhman, Prog. Chem., 19, 265 (1950).

---

* See Consultants Bureau Translation, p. 967.

MACROMOLECULAR COMPOUNDS

COMMUNICATION 70. PECULIAR FEATURES OF CHAIN GROWTH DURING POLYCONDENSATION IN PRESENCE OF A CATALYST*

G. S. Kolesnikov, V. V. Korshak and T. V. Smirnova

One of us, in conjunction with Rafikov and Zamyatina [1], has shown that the process of polycondensation is a very complex equilibrium system of reversible reactions. Simultaneously with the chain-growth reaction, which leads to the formation of linear polycondensation products of various molecular weights [2, 4], there occurs also the reverse process – i.e. the destruction of the macromolecular compounds formed by the starting substances – by reaction products of low molecular weight, and by polycondensation products of various molecular weights (dimers, trimers, etc.). It has been established, for example, that polyamides are degraded by carboxylic acids and amines [3], and polyesters are degraded by carboxylic acids, alcohols, and glycols [4].

The rates of the chain-growth and degradation reactions change during the polycondensation process. At the beginning of the process the rate of chain growth greatly exceeds the rate of degradation, but as the polycondensation proceeds the rate of chain growth falls and the rate of degradation rises, so that these rates finally become equal, and a condition of equilibrium is attained. The growth of the polymer molecules then ceases and the molecular weight of the polycondensation products does not rise. The position of equilibrium therefore determines the molecular weight of the final polycondensation products.

Processes of polycondensation and degradation have been studied fairly thoroughly from the point of view of the effect of the nature of the reactants and their proportions [2-5], but the part played by the catalyst in polycondensation processes has not yet been fully elucidated. These processes often occur at high temperatures and in presence of catalysts; or the components themselves may act as catalysts, as acids and glycols do in polyesterification [6]. As would be expected, the choice of catalyst and its concentration are not matters of indifference in polycondensation processes, since the action of the catalyst on different components of the reaction system will be different, and so may affect the position of equilibrium, displacing it in one direction or the other and so determining the molecular weight of the polycondensation products. We have, therefore, investigated the effect of the catalyst on the chain growth of the product of the polycondensation of 1,2-dichloroethane with benzene in presence of aluminum chloride.

We have previously studied [5] the effect of the proportions of the reactants on the properties of the products of the polycondensation of 1,2-dichloroethane with benzene in presence of aluminum chloride. It was found that the molecular weight of poly(ethylenephenyl), the macromolecular product of this polycondensation, increases as the excess of benzene falls. By analogy with other polycondensation reactions it may be supposed that in the polycondensation of 1,2-dichloroethane with benzene, which is always carried out in presence of a catalyst, the formation of poly(ethylenephenyl) will be accompanied by a reaction leading to its degradation. The molecular weight of the poly(ethylenephenyl) obtained will be determined by the position of equilibrium, which, in its turn, will depend not only on the proportions of the reactants, but probably also on the amount of catalyst, since a variation in this amount will affect its concentration in the reaction system, and will therefore alter the rate of degradation and the overall rate of the process. The main reactions occurring in the polycondensation of 1,2-dichloroethane with benzene are as follows:

$$n\mathrm{ClCH_2CH_2Cl} + (n+1)\mathrm{C_6H_6} \xrightarrow{\mathrm{AlCl_3}} \mathrm{C_6H_5(CH_2CH_2C_6H_4)_nH} + 2n\mathrm{HCl}.$$

$$\mathrm{C_6H_5(CH_2CH_2C_6H_4)_nH} + m\mathrm{C_6H_6} \xrightarrow{\mathrm{AlCl_3}} (m+1)\,\mathrm{C_6H_5(CH_2CH_2C_6H_4)_{n/m+1}H}$$

The experimental procedure was the same as that used previously [5]. Several series of experiments were carried out, and in each series the proportions of reactants and the reaction conditions remained constant, but the amount of catalyst was varied. The results are given in Tables 1-4. In these tables the amount of aluminum chloride used is expressed as a molar percentage of the amount of 1,2-dichloroethane.

It will be seen from Tables 1-4 that, in order to obtain a poly(ethylenephenyl) of maximum molecular weight, a definite amount of aluminum chloride must be used for each ratio of the reactants. The use of lower amounts of aluminum chloride either results in low yields of condensation products of low molecular weight, or prevents reaction from occurring.

---

* This is also Communication 12 of the series, "The Mechanism of the Friedel-Crafts Reaction."

TABLE 1

Polycondensation of 1,2-Dichloroethane with Benzene (Benzene : dichloroethane = 1.2)

Aluminum chloride (mole-%)	Yield (%) of			Mol. wt. of poly(ethylenephenyl)
	Bibenzyl	p-bis(2-phenylethyl) benzene	poly(ethylenephenyl)	
0.53	Reaction did not go			
1.06	Reaction did not go			
1.59	6.2	3.5	5.4	1460
2.12	8.4	4.2	8.9	1750
2.65	1.8	1.3	42.2	6740
3.58	2.5	2.7	74.8	6450
5.30	3.7	2.9	56.8	3340

TABLE 2

Polycondensation of 1,2-Dichloroethane with Benzene (Benzene : dichloroethane = 1.3)

Aluminum chloride (mole-%)	Yield (%) of			Mol. wt. of poly(ethylenephenyl)
	Bibenzyl	p-bis(2-phenylethyl) benzene	poly(ethylenephenyl)	
0.58	Reaction did not go			
1.15	6.3	4.6	39.5	3040
1.73	3.4	3.0	45.4	4220
2.30	4.0	4.6	66.4	3600
2.88	4.0	4.6	65.6	3650
3.89	4.0	2.5	73.5	4020
5.76	4.1	4.5	74.4	3280

TABLE 3

Polycondensation of 1,2-Dichloroethane with Benzene (Benzene : dichloroethane = 1.5)

Aluminum chloride (mole-%)	Yield (%) of			Mol. wt. of poly(ethylenephenyl)
	Bibenzyl	p-bis(2-phenylethyl) benzene	poly(ethylenephenyl)	
0.66	Reaction did not go			
1.33	6.8	5.6	65.8	3310
1.66	6.8	5.6	61.2	3100
1.99	7.3	6.2	71.4	2760
2.65	7.3	6.5	70.5	3080
3.32	6.6	5.9	64.6	2590
4.47	6.8	7.4	68.0	2620
6.63	3.6	0.9	75.5	1880

TABLE 4

Polycondensation of 1,2-Dichloroethane with Benzene (Benzene : dichloroethane = 2.0)

Aluminum chloride (mole-%)	Yield (%) of			Mol. wt. of poly(ethylenephenyl)
	Bibenzyl	p-bis(2-phenylethyl)benzene	poly(ethylenephenyl)	
0.88	Reaction did not go			
1.77	3.2	5.8	27.2	3010
2.65	16.8	12.4	60.0	2430
3.53	17.5	8.0	69.2	2740
4.41	14.3	12.1	53.8	2200
5.96	12.6	11.5	52.2	2100

The use of more than the optimum amount of aluminum chloride results in a reduction in the molecular weight of the poly(ethylenephenyl), but does not affect its yield appreciably. The effect of the amount of aluminum chloride taken on the molecular weight of the poly(ethylenephenyl) is particularly notable when the molar ratio of benzene to dichloroethane is 1.20. When the amount of aluminum chloride is less than 2.6 mole-% of the amount of 1,2-dichloroethane taken, polycondensation either does not occur, or results in the formation of a poly(ethylenephenyl) of low molecular weight in low yield. Increase in the amount of aluminum chloride beyond 4.0-4.5 mole-% on the amount of dichloroethane taken results in a sharp reduction in the molecular weight of the poly(ethylenephenyl).

Our results are probably to be explained as follows. The first stage of the polycondensation of 1,2-dichloroethane with benzene in presence of aluminum chloride is probably the formation of a complex compound of aluminum chloride with 1,2-dichloroethane:

$$ClCH_2CH_2Cl + Al_2Cl_6 \rightleftharpoons ClCH_2CH_2Cl \cdot Al_2Cl_6.$$

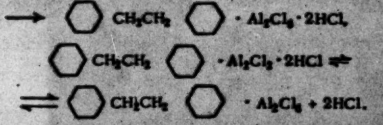
The composition of this complex must actually be less simple, $nClCH_2CH_2Cl \cdot mAl_2Cl_6$ for example, as was shown by one of us and Lebedev [7]. However, for simplicity of exposition, we shall assume the simplest composition $ClCH_2CH_2Cl \cdot Al_2Cl_6$ for the complex, for, in this way, we shall be able to represent the processes occurring during polycondensation more clearly, without distorting in any way the principle upon which our explanation is based. The complex $ClCH_2CH_2Cl \cdot Al_2Cl_6$ reacts further with benzene, forming a ternary complex:

$$ClCH_2CH_2Cl \cdot Al_2Cl_6 + 2C_6H_6 \rightleftharpoons$$
$$\rightleftharpoons ClCH_2CH_2Cl \cdot Al_2Cl_6 \cdot 2C_6H_6.$$

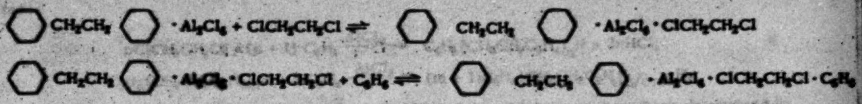
The formation of ternary complexes consisting of an aromatic hydrocarbon, an alkyl halide, and aluminum halide, has been proved by one of us, working with Lebedev and Fedoseev [8].

Reaction between 1,2-dichloroethane and benzene occurs within the ternary complex, and results in the formation of the ternary complex bibenzyl—aluminum chloride—hydrogen chloride:

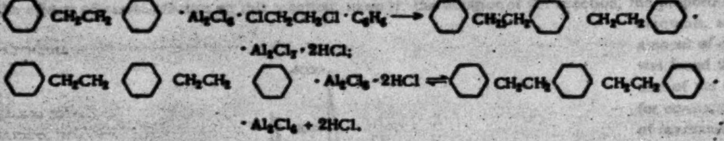
$$ClCH_2CH_2Cl \cdot Al_2Cl_6 \cdot 2C_6H_6 \longrightarrow$$



The complex compound of bibenzyl with aluminum chloride again reacts with dichloroethane and benzene:


CH₂CH₂ · Al₂Cl₆ + ClCH₂CH₂Cl ⇌ CH₂CH₂ · Al₂Cl₆ · ClCH₂CH₂Cl
CH₂CH₂ · Al₂Cl₆ · ClCH₂CH₂Cl + C₆H₆ ⇌ CH₂CH₂ · Al₂Cl₆ · ClCH₂CH₂Cl · C₆H₆

Reaction occurs within the complex, and results in the formation of a long chain, hydrogen chloride being evolved:


CH₂CH₂ · Al₂Cl₆ · ClCH₂CH₂Cl · C₆H₆ ⟶ CH₂CH₂ CH₂CH₂ ·
· Al₂Cl₆ · 2HCl;
CH₂CH₂ CH₂CH₂ · Al₂Cl₆ · 2HCl ⇌ CH₂CH₂ CH₂CH₂ ·
· Al₂Cl₆ + 2HCl.

Further lengthening of the chain occurs in a similar way. In order that the equilibrium

$$ClCH_2CH_2Cl \cdot Al_2Cl_6 + 2C_6H_6 \rightleftharpoons ClCH_2CH_2Cl \cdot Al_2Cl_6 \cdot 2C_6H_6$$

may be displaced to the right to the extent necessary for the amount of ternary complex to be sufficient for rapid reaction within the complex, there must be a sufficiently large excess of one of the original components. When the excess of benzene is small, a definite, fairly large excess of the complex $ClCH_2CH_2Cl \cdot Al_2Cl_6$, must be present in order that the displacement of the equilibrium to the right may be sufficiently large. In its turn, the amount of the complex $ClCH_2CH_2Cl \cdot Al_2Cl_6$ depends entirely on the amount of aluminum chloride, so that for a sufficiently large displacement of the equilibrium to the right, a fairly large amount of aluminum chloride must be used. These considerations are fully in accord with the experimental results. When the excess of benzene is increased, the same shift in the equilibrium to the right may be obtained in presence of a smaller amount of the complex $ClCH_2CH_2Cl \cdot Al_2Cl_6$ than that required in the case considered above. In other words, as the excess of benzene in the mixture of reactants is increased, the amount of aluminum chloride needed for the same shift in the equilibrium will diminish. The experimental results are in good agreement with this conclusion:

TABLE 5

Kinetics of the Degradation of Poly(ethylenephenyl) by Benzene

Duration of degradation (hours)	Yield of poly(ethylenephenyl) (% on weight of original poly(ethylenephenyl)	Mol. wt. of poly(ethylenephenyl)
0	100	3860
1	91	3310
2	78	1820
3	50	1720
5	25	1650
7	23	1280

TABLE 6

Dependence of the Degradation of Poly(ethylenephenyl) on the Amount of Benzene

Proportion by wt. of benzene to poly(ethylenephenyl)	Yield of poly(ethylenephenyl) [% on wt. of original poly(ethylenephenyl)]	Mol. wt. of poly(ethylenephenyl)
0.00	100	3860
0.88	70	2420
2.2	40	2070
4.4	27	2140
8.8	25	1650

It will be seen from Tables 1-4 that the smallest amount of aluminum chloride for the formation of a poly(ethylenephenyl) of high molecular weight in satisfactory yield falls in value as the ratio benzene : dichloroethane increases. We consider that the proposed explanation of the course of the reaction is confirmed by the absence of any reaction between 1,2-dichloroethane and benzene in presence of aluminum chloride when the proportions of reactants are dichloroethane : : benzene : aluminum chloride = 2.0 : 0.205 : 0.00615. It is probable that in this case the amounts of aluminum chloride and benzene are insufficient for the formation of the ternary complex $ClCH_2CH_2Cl \cdot Al_2Cl_6 \cdot 2C_6H_6$ in sufficient amount to enable reaction between dichloroethane and benzene to proceed at an appreciable rate.

The amount of aluminum chloride, however, cannot be increased beyond a certain limit without reduction in the molecular weight of the poly(ethylenephenyl) formed. The cause of this reduction in molecular weight may be the degradation of poly(ethylenephenyl) by benzene, which is present in excess, since, under these conditions, two reactions may occur simultaneously: the polycondensation of 1,2-dichloroethane with benzene, and the degradation of poly(ethylenephenyl) by benzene:

$$nClCH_2CH_2Cl + (n+1)\,C_6H_6 \xrightarrow{AlCl_3} C_6H_5[CH_2CH_2C_6H_4]_nH + 2nHCl;$$

$$C_6H_5[CH_2CH_2C_6H_4]_nH + mC_6H_6 \xrightarrow{AlCl_3} (m+1)C_6H_5[CH_2CH_2C_6H_4]_{n/m+1}H.$$

Some of the laws governing the polycondensation of 1,2-dichloroethane with benzene have been determined by us previously [5]. In order to discover the main laws governing the degradation of poly(ethylenephenyl) by benzene, we have studied the effects of various factors on this reaction, namely, the duration of the reaction, the proportions of the reactants, and the amount of catalyst. It was found that the extent of the degradation for constant proportions of reactants and a constant amount of aluminum chloride depends on the duration of the reaction: the amount of poly(ethylenephenyl) present falls and its molecular weight diminishes, and, simultaneously, the amount of bibenzyl, the reaction product of lowest molecular weight, rises (Table 5, and Fig. 1) (ratio benzene : : poly(ethylenephenyl) = = 8.8 : 1; the concentration of aluminum chloride was 50% on the weight of poly(ethylenephenyl)).

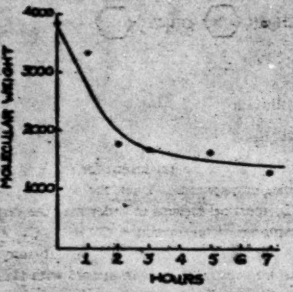


Fig. 1. Kinetics of the degradation of poly(ethylenephenyl) by benzene.

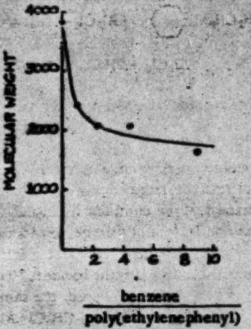


Fig. 2. Effect of the amount of degrading substance (benzene) on the mol. wt. of poly(ethylenephenyl)

A study of the effect of the proportions of reactants, the amount of catalyst and duration of reaction being constant, showed that in this case, as in that of polyamides and polyesters [4], increase in the amount of degrading substance results in a reduction in the amount of poly (ethylenephenyl) and a lowering of its molecular weight. The results of this study are shown in Table 6 and Figures 2 and 3 (the concentration of aluminum chloride was 50% on the weight of poly(ethylenephenyl), and the duration of the reaction was five hours).

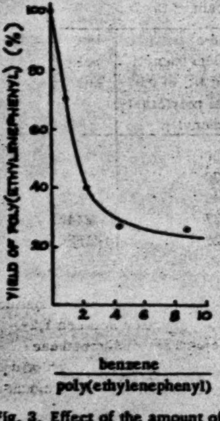


Fig. 3. Effect of the amount of degrading substance (benzene) on the yield of poly(ethylenephenyl).

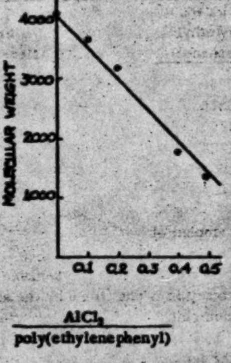


Fig. 4. Effect of the concentration of the degradation catalyst on the mol. wt. of poly(ethylenephenyl)

It will be seen from Table 6 and Fig. 2 that a great reduction in molecular weight is produced by the action of only small amounts of benzene. A further increase in the amount of benzene has less effect on the molecular weight, which is the usual behavior in degradation reactions [9]. The amount of catalyst used also affects the molecular weight of the poly(ethylenephenyl) and the yield of degradation products. Results of experiments carried out for constant proportions of reactants and for a constant reaction time, but with varying amounts of aluminum chloride, are shown in Table 7 and Fig. 4 (for a reaction time of seven hours).

Table 7 and Fig. 4 show that, as the amount of aluminum chloride is increased, the extent of degradation increases with a resulting fall in the molecular weight of poly(ethylenephenyl). It is clear, therefore, why a reduction was observed in the molecular weight of the poly(ethylenephenyl) obtained when the amount of aluminum chloride was increased beyond its optimum value. This change will result not only in an increase in the concentration of the ternary complex, but also in an increase in the number of degradation centers, so that a poly(ethylenephenyl) of lower molecular weight is obtained. It may, therefore, be regarded as established that the polycondensation of 1,2-dichloroethane with benzene in presence of aluminum chloride is a reversible one, and the position of equilibrium depends on the relative amounts of all components of the reaction system.

TABLE 7

Dependence of the Degradation of Poly (ethylenephenyl) on the Amount of Aluminum Chloride)
[Benzene: poly(ethylenephenyl) = 8.8 (by weight)]

Ratio of aluminum chloride to poly(ethylenephenyl) (by wt.)	Yield of poly (ethylenephenyl) [% by wt. on original poly(ethylenephenyl)]	Molecular wt. of the poly (ethylenephenyl)
0.0	100	4070
0.1	73	3660
0.2	75	3190
0.4	50	1780
0.5	17.5	1420

SUMMARY

1. It has been shown that the polycondensation of 1,2-dichloroethane with benzene in presence of aluminum chloride is a reversible reaction, the position of equilibrium being determined by the relative amounts of all of the starting substances.

2. It has been shown that poly(ethylenephenyl) is degraded by benzene in presence of aluminum chloride. The laws governing this reaction have been determined.

LITERATURE CITED

[1] V. V. Korshak, S. R. Rafikov, and V. A. Zamyatina, Investigations on Macromolecular Compounds, Acad. Sci. U.S.S.R. Press, Moscow and Leningrad, 1949, p. 3.

[2] V. V. Korshak and S. R. Rafikov, J. Gen. Chem. 14, 974 (1944).

[3] V. V. Korshak and V. A. Zamyatina, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., 1945, No. 6, 609.

[4] S. R. Rafikov, V. V. Korshak, and G. N. Chelnokova, Proc. Acad. Sci. U.S.S.R., 57, 347 (1947).

[5] G. S. Kolesnikov, V. V. Korshak, and T. V. Smirnova, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., 1951, No. 5, 596.

[6] V. V. Korshak and S. V. Vinogradova, Proc. Acad. Sci. U.S.S.R., 77, 277 (1951).

[7] V. V. Korshak and N. N. Lebedev, Proc. Acad. Sci. U.S.S.R., 57, 263 (1947).

[8] V. V. Korshak, N. N. Lebedev, and S. D. Fedoseev, J. Gen. Chem., 17, 575 (1947).

[9] V. V. Korshak, Proc. Acad. Sci. U.S.S.R., 64, 525 (1949).

BLANK
PAGE

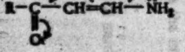
BRIEF COMMUNICATIONS

2-AMINOVINYL KETONES

COMMUNICATION 2. SYNTHESIS OF ALKYL 2-AMINOVINYL KETONES

A. N. Nesmeyanov, N. K. Kochetkov, and Ya. V. Dombrovsky

In previous investigations carried out in our laboratory it has been shown that many possibilities exist for syntheses based on the readily available alkyl 2-chlorovinyl ketones. There can be no doubt that the investigation of alkyl 2-aminovinyl ketones is also of interest in this respect. These compounds are also of theoretical interest, since the conjugation of the carbonyl with the double bond and the free pair of electrons on the nitrogen


$$R-\underset{\underset{O}{\|}}{C}-CH{=}CH-\ddot{N}H_2$$

would be expected to affect their chemical and physical properties. These compounds may also be found to have practical interest: thus, the use of alkyl 2-aminovinyl ketones as antidetonators has been described [1].

There has been no satisfactory method for the preparation of alkyl 2-aminovinyl ketones. The method based on the action of ammonium salts on 2-hydroxyvinyl ketones [2] cannot be regarded as general, owing to the poor accessibility of these ketones; also, the reaction is often accompanied by the formation of pyridine derivatives, so that the yield of the aminovinyl ketone is greatly reduced [3, 4]. The preparation of alkyl 2-aminovinyl ketones from the corresponding alkyl 2-chlorovinyl ketones by the action of ammonia in anhydrous solvents has been described in the patent literature [5, 6]. After numerous experiments under these conditions, we are convinced that yields of not more than 25% of aminovinyl ketone can be obtained by this method.

We have succeeded in working out a modified method for the synthesis of alkyl 2-aminovinyl ketones from 2-chlorovinyl ketones which makes it possible to prepare them in high yield (78 - 84%). This was achieved by carrying out the reaction in concentrated aqueous ammonia and continuing to maintain the high concentration of ammonia by continuous saturation of the reaction mixture with gaseous ammonia. This method makes alkyl 2-aminovinyl ketones readily accessible and makes it possible for them to be applied in organic synthesis. Such application will form the object of our further investigations.

Alkyl 2-aminovinyl ketones are high-boiling, colorless oils, which gradually turn yellow. The exaltation of molecular refraction is 3.36-3.55 units for these compounds, which is somewhat lower than the values for alkyl 2-dialkylaminovinyl ketones, which were recently prepared by one of us [7].

All of the alkyl 2-aminovinyl ketones that we have prepared have one very interesting property: the refractive index of the freshly distilled substance rapidly increases until it reaches a limiting value after about 90 minutes. For example, the refractive index of 2-aminovinyl methyl ketone (4-amino-3-buten-2-one) changes from n_D^{20} 1.5462 to n_D^{20} 1.5668. When the sample is redistilled, the refractive index reverts to the lower value and then changes over the same range. It is probable that a tautomeric change occurs, and we are at present investigating the nature of this change.

EXPERIMENTAL

Gaseous ammonia was passed into 600 ml of 25% aqueous ammonia cooled to 0-3° so as to maintain the solution saturated while the alkyl 2-chlorovinyl ketone (0.2 mole) was added dropwise over a period of 20 minutes, the mixture being vigorously stirred and cooled. Stirring was continued for a further two hours, and the mixture was then left in an ice bath for a few hours. The solution was saturated with potassium carbonate and extracted several times with ether (it is best to extract the methyl and ethyl homologs in a liquid extractor). The extract was dried with potassium carbonate, the ether was distilled off, and the residue was vacuum-distilled. The yields, constants, and results of elementary analysis are given in the table for the synthesized alkyl 2-aminovinyl ketones.

Synthesis and Properties of Alkyl β-Aminovinyl Ketones $R-CO-CH=CH-NH_2$

R	Yield (%)	B.p. in °C (p in mm Hg)	n_D^{20} *	d_4^{20}	MR		E_{MR}	Carbon (in %)		Hydrogen (in %)	
					Found	Calc'd		Found	Calc'd	Found	Calc'd
CH_3	84,4 **	70 - 71 (3)	1,5668	1,0220	27,19	23,64	3.55	56.53 56.51	56.45	8.51 8.42	8.29
C_2H_5	77.8	72 - 73 (3)	1.5440	0.9893	31.62	28.26	3.36	60.88 60.74	60.59	9.37 9.19	9.15
$n-C_3H_7$	81.8	84 - 85 (3)	1.5327	0.9650	36.40	32.87	3.53	63.37 63.50	63.64	9.84 9.96	9.79
$(CH_3)_2CH$	80.2	55 - 56 (0.5)	1.5273	0.9610	36.24	32.87	3.37	63.31 63.52	63.64	9.71 9.72	9.79
$(CH_3)_2CH_2CH$	83.5	98 - 99 (2.5)	1.5221	0.9456	41.03	37.49	3.54	66.10 66.21	66.10	10.38 10.33	10.30
$n-C_5H_{11}$	79.6	103 (2)	1.5160	0.9342	45.65	42.10	3.55	68.05 68.24	68.11	10.88 10.71	10.72

* The values given for the refractive index are the maximum values, measured after the substance has been allowed to stand for two hours.

** The yield is not reduced when the synthesis is carried out on a larger scale (about two moles of the chlorovinyl ketone).

LITERATURE CITED

[1] French Pat. 720619; C., 1932, II, 486.

[2] E. Benary, Ber., 63B, 1573 (1930).

[3] E. Benary, H. Psille, Ber., 57, 828 (1924).

[4] E. Benary, Ber. 60, 914 (1927).

[5] French Pat. 840107; C. 1939, II, 3193.

[6] U.S. Pat. 2198260; C.A. 34, 5463 (1940).

[7] N. K. Kochetkov, Bull. Acad. Sci., USSR Div. Chem. Sci., 1953, No. 6, 991.*

Received October 27, 1954

M. V. Lomonosov Moscow State University

---

* See Consultants Bureau Translation, p. 883.

REACTION OF 3-BUTEN-1-YNYLMAGNESIUM BROMIDE WITH HALOTRIPHENYLSILANES

A. D. Petrov, S. I. Sadykhzade, and V. M. Vdovin

A study of the organomagnesium synthesis of 3-buten-1-ynylsilanes [1] has led us to the discovery of considerable difference between the syntheses of trialkyl-(and triphenyl-)3-buten-1-ynylsilanes and those of the corresponding trialkyl-(and triphenyl-)3-buten-1-ynylmethanes. It was found that, whereas the very reactive $(C_6H_5)_3C\cdot Cl$ condenses with $CH_2{=}CH{-}C{\equiv}C\cdot MgBr$ [2], its structural analog $(C_6H_5)_3SiCl$ does not react with the reagent. On the other hand $(CH_3)_3SiCl$ condenses with $BrMgC{\equiv}C{-}CH{=}CH_2$, giving high yields of product, whereas the carbon analog of this chlorosilane $(CH_3)_3C\cdot Cl$ does not react with this Grignard reagent.

With the object of elucidating the causes of this behavior of chlorotriphenylsilanes in synthesis, and also of overcoming the obstacles to the use of compounds containing triphenylsilyl radicals, we have followed two courses: a) introduction into the phenyl radical of a substituent having a positive Hammett constant (for this purpose chlorine was taken; for chlorine $\sigma = +0.227$ [3]); and b) the replacement of chlorine by fluorine in $(C_6H_5)_3SiCl$.

The idea of replacing chlorine by fluorine was suggested by the fact that the degree of ionization of the $Si{-}F$ bond is considerably higher than that of the $Si{-}Cl$ bond [4]. (By taking advantage of this fact, Petrov and Chernysheva [5] were recently able to overcome considerable steric difficulties and effect the syntheses of tetraisopropylsilane, tetracyclohexylsilane, and tetra-1-naphthylsilane.) Both courses led to positive results, and we have synthesized $p\text{-}(ClC_6H_4)_3Si{-}C{\equiv}C{-}CH{=}CH_2$ and $(C_6H_5)_3Si{-}C{\equiv}C{-}CH{=}CH_2$, for the first time.

Thus, the difference in reactivity between $(C_6H_5)_3SiCl$ and $(C_6H_5)_3CCl$ is apparently due both to the difference in electron density between the bonds of these siliconium and carbonium radicals with chlorine, and also to the greater steric difficulties in the formation of the siliconium ion.

EXPERIMENTAL

1. 3-Buten-1-ynyltriphenylsilane $(C_6H_5)_3Si{-}C{\equiv}C\cdot CH{=}CH_2$. To $CH_2{=}CH{-}C{\equiv}C\cdot MgBr$, prepared from 12 g of Mg, 54.5 g of C_2H_5Br, and 50 g of $HC{\equiv}C\cdot CH{=}CH_2$, 40 g $(C_6H_5)_3SiF$ was added. The last compound was obtained from C_6H_5MgBr and SiF_4; b.p. 207-210°/12 mm; m.p. 60° (for this compound Medoks and Kotelkov [6] give m.p. 64° and b.p. 200-210°/19 mm. When the $(C_6H_5)_3SiF$ was added to the $CH_2{=}CH{-}C{\equiv}CMgBr$ no change could be observed in the reaction mass. The contents of the flask were heated and stirred for two hours, the diluent being diethyl ether. The diethyl ether was replaced by dibutyl ether, and heating was then continued at 80° for eight hours. The product was 38 g (84.5 %) of a substance of m.p. 93°.

Found %: H 5.94; C 85.09: Si 9.27
$C_{22}H_{18}Si$. Calculated %: H 5.81; C 85.01: Si 9.03

2. Chlorotris-(p-chlorophenyl) silane $(ClC_6H_4)_3SiCl$. 1-Bromo-4-chlorobenzene (280 g) was dissolved in ether and added over a period of six hours to a stirred mixture of 40 g of magnesium and 700 ml of ether. Much heat was evolved, and the ether boiled. The resulting Grignard reagent was then added to 70 g of $SiCl_4$. This reaction was also accompanied by the evolution of heat. The reaction mixture was heated for five hours at the boiling point of ether. Ether was then removed, and the mixture was heated for eight hours in a water bath. Fractionation of the residue yielded 25 g (12.5%) of a thick oil, b.p. 242-243°/3 mm, which solidified as a glass, on standing.

Found %: Si 6.88
$C_{18}H_{12}SiCl_4$. Calculated %: Si 7.05

3. 3-Buten-1-ynyltris (p-chlorophenyl)silane $(ClC_6H_4)_3Si{-}C{\equiv}C\cdot CH{=}CH_2$. From 10 g of $(ClC_6H_4)_3SiCl$ and excess of the Grignard reagent $(CH_2{=}CH{-}C{\equiv}C{-}MgBr)$ 3.5 g (30%) of a crystalline substance of m.p. 107-108° was obtained.

Found %: Si 6.70
$C_{22}H_{15}SiCl_3$. Calculated %: Si 6.75

LITERATURE CITED

[1] A. D. Petrov and S. M. Sadykhzade, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., 1954, 4, 722.

[2] W. Carothers, S. Berchet, J. Am. Chem. Soc. 55, 1094 (1933).

[3] L. Hammett, Physical Organic Chemistry, 1940, p. 188. McGraw Hill Book Co., N. Y.

[4] H. Gilman, G. Dunn, Chem. Rev. 52, 77 (1953)

[5] A. D. Petrov and T. I. Chernyshova, J. Gen. Chem., 24 (1954). *

[6] G. E. Meddis and N. Z. Kotelkov, J. Gen. Chem., 7, 2007 (1937).

Received July 22, 1954

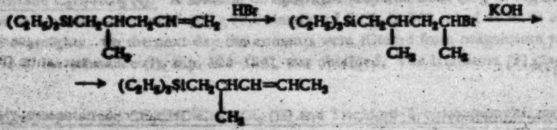
N. D. Zelinsky Institute of Organic
Chemistry of the U.S.S.R. Academy of Sciences

SYNTHESIS OF 3- AND 4-ALKENYLTRIALKYLSILANES

V. F. Mironov and N. A. Pogonkina

It can be considered that it is now firmly established that hydrogen halides add to various organosilicon compounds containing the vinyl radical in the direction contrary to that required by Markovnikov's rule [1], whereas they add to allyl derivatives solely in the direction required by the rule [2], even in presence of a peroxide [3].

In the present investigation we have proved the direction of the addition of HBr to a 4-alkenylsilane with the aid of the following reactions:

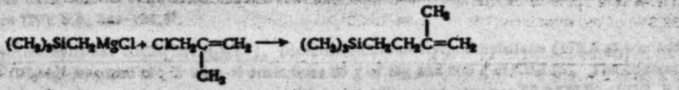


$$(C_2H_5)_3SiCH_2\underset{CH_3}{\underset{|}{C}}HCH_2CH{=}CH_2 \xrightarrow{HBr} (C_2H_5)_3SiCH_2\underset{CH_3}{\underset{|}{C}}HCH_2\underset{CH_3}{\underset{|}{C}}HBr \xrightarrow{KOH} (C_2H_5)_3SiCH_2\underset{CH_3}{\underset{|}{C}}HCH{=}CHCH_3 \qquad (1)$$

The difference between the original 4-alkenylsilane and the 3-alkenylsilane formed was established by a comparison of their Raman spectra. Petrov and Nikishin [4] have proposed another method for the preparation of 3-alkenylsilanes. They have synthesized 3-butenyltrimethylsilane (Equation 2), and have shown that HBr adds to this compound in accordance with Markovnikov's rule:

$$(CH_3)_3SiCH_2MgCl + BrCH_2CH{=}CH_2 \longrightarrow (CH_3)_3SiCH_2CH_2CH{=}CH_2 \qquad (2)$$

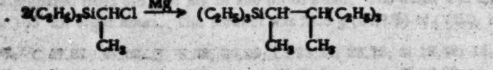
By this scheme (Equation 2) we have obtained four new 3-alkenylsilanes, including the first 3-alkenylsilane having a double bond at a tertiary carbon:



$$(CH_3)_3SiCH_2MgCl + ClCH_2\underset{CH_3}{\underset{|}{C}}{=}CH_2 \longrightarrow (CH_3)_3SiCH_2CH_2\overset{CH_3}{\overset{|}{C}}{=}CH_2$$

The various trialkyl-1-chloroalkylsilanes (α-chlorides) required as starting materials were synthesized by the action of Grignard reagents on chloro-(1-chloroalkyl)silanes, which have now become accessible [5, 11].

Grignard reagents are obtained from α-chlorides in high yield. From $(C_2H_5)_3SiCHClCH_3$, however, in addition to RMgX, a considerable amount of dimerization product is obtained:



$$2(C_2H_5)_3Si\underset{CH_3}{\underset{|}{C}}HCl \xrightarrow{Mg} (C_2H_5)_3Si\underset{CH_3}{\underset{|}{C}}H{-}\underset{CH_3}{\underset{|}{C}}H(C_2H_5)_3$$

Hence, for the preparation of RMgX from this α-chloride, it is necessary to pour it slowly (100-150 drops/minute) into a 1.5-2-fold excess of magnesium. This tendency for the secondary α-chloride to undergo condensation during the preparation of RMgX is to be associated with analogous properties noted previously by Petrov and Mironov [2] for β- and δ-halides. Molecular refractions calculated from the component values proposed by Warrick [6] show exaltations for our compounds, and these increase as the number of ethyl groups on the silicon atom increase. In order to find a more precise value for the refraction of an Si−C bond in which the C belongs to an ethyl radical, we made use of reliable constants for the alkyltriethylsilane series [7]. It was found that for this series the molecular refraction differs from the calculated value by 0.64% on the average. If, however, the refraction of Si−C in which the C belongs to ethyl is taken to be 2.38 ml/mole instead of the standard value 2.50 [6], the discrepancy is reduced to 0.1%. For convenience in calculation, and also so that it is unnecessary to make an assumption relating the exaltation to a particular bond of the ethyl radical (i.e., to assume which particular bond is polarized), it is desirable to use a value for the refraction of the group $Si-C_2H_5$, namely 12.08

ml/mole. Results obtained by use of this value in molecular-refraction calculations are given in the table, in which the constants for $(C_2H_5)_3SiCH{=}CH_2$, which have been redetermined by us, are also given.

In the present investigation we have prepared the first 5-alkenylsilane:

$$(CH_3)_3SiCH_2CH_2CH_2MgBr + BrC_3H_5 \longrightarrow (CH_3)_3SiCH_2CH_2CH_2CH_2CH{=}CH_2$$

The γ-halide required for this purpose was prepared from $(CH_3)SiCH_2CH_2CH_2OH$ [8], or by the chlorination of trichloropropylsilane. In the only description of the chlorination of $C_3H_7SiCl_3$ given in the literature, SO_2Cl_2 is used [9]. We chlorinated $C_3H_7SiCl_3$ in an apparatus such that the chlorination would actually occur in the liquid phase but the chlorinated product would be removed from the chlorination zone in order to reduce the amount of polychlorides formed [5]. Under these conditions practically no trichloro-1-chloropropylsilane was formed from $C_3H_7SiCl_3$, and the 2- and 3-chloro isomers were formed in ratio 1 : 0.6. When $C_3H_7SiCl_3$ is chlorinated with sulfuryl chloride [9], the 1-, 2-, and 3-isomers are formed in the proportions of 1 : 3.5 : 3.1.

EXPERIMENTAL

Trichloropropylsilane $C_3H_7SiCl_3$ (I). A solution of C_3H_7MgBr prepared from 61 g of Mg (2.51 mole) in 1 liter of ether was added to a cooled solution of 500 g (2.94 mole) of $SiCl_4$ in 500 ml of ether in a 2-liter flask. The flask was set aside overnight. On the next day the contents were filtered from magnesium salts and fractionated, and 275 g (61.5%) of the substance (I), b.p. 123-124°, was obtained. The literature [9] gives b.p. 122-124°, and yield 41%.

Trichloro-2-chloropropylsilane $CH_3CHClCH_2SiCl_3$ (II) and Trichloro-3-chloropropylsilane $ClCH_2CH_2CH_2SiCl_3$ (III.) The substance (I) (274 g) was placed in the flask of the apparatus already described [5]. Chlorination was continued until the temperature in the flask reached 152°, which required seven hours. The rate of passage of chlorine was 200 bubbles per minute. Fractionation through a 30-plate column yielded 90 g of substance (I), b.p. 123°, 114 g of (II), b.p. 162°, and 63.3 g of (III), b.p. 181.5°. The combined yield of (II) and (III) was 81% on the amount of (I) that reacted.

2,2,4,4-Tetramethyl-2,4-disilapentane [10] $(CH_3)_3SiCH_2Si(CH_3)_3$ (IV). 1,1,1,3,3,3-Hexachloro-1,3-disilapropane (142 g) was added dropwise to a cooled solution of CH_3MgI prepared in 1 liter of ether from 94 g of Mg and 600 g of CH_3I. The ether was removed, and the residue was heated in a boiling water bath for four hours. The ether was returned to the flask, and decomposition was effected with water and HCl. The product was 69.5 g (86.3%) of the substance (IV), b.p. 134-134.3°.

(Chloromethyl)trimethylsilane $ClCH_2Si(CH_3)_3$ (V). Dichloro(chloromethyl)methylsilane (163.5 g) was added to a cooled solution of CH_3MgI prepared in 1 liter of ether from 55 g of Mg and 350 g of CH_3I [5]. The contents of the flask were boiled for five hours and then decomposed with water. The products were 93 g (76%) of (V), b.p. 98.5°/765 mm, and 11 g (9%) of (iodomethyl)trimethylsilane [5]. The α-chlorides that follow, and also (chloromethyl)ethyldimethylsilane (VI) and (chloromethyl)diethylmethylsilane (VII), were prepared under similar conditions.

(Chloromethyl)dimethylpropylsilane $ClCH_2SiC_3H_7(CH_3)_2$ (VIII). Chloro(chloromethyl)dimethylsilane [5] (38.4 g) was added to C_3H_7MgCl prepared from 6.5 g of Mg in 250 ml of ether. The ether was distilled off, and the mixture was heated at about 100° for eight hours. The product was 22.3 g (55.7%) of (VIII), b.p. 150-151.8°.

Found %: C 47.81; 48.00; H 9.98; 10.09; Cl 23.21; 23.75; Si 18.48; 18.33
$C_6H_{15}SiCl$. Calculated %: C 47.82; H 10.03; Cl 23.53; Si 18.62

(Chloromethyl)methyldipropylsilane $ClCH_2Si(C_3H_7)_2CH_3$ (IX). To C_3H_7MgBr, prepared from 24 g of Mg in 500 ml of ether, 70 g of dichloro(chloromethyl)methylsilane [5] was added. Boiling was for six hours. The product was 54 g (70%) of (IX), b.p. 190-192°.

Found %: C 53.73; 53.46; H 10.50; 10.51; Cl 19.40; 19.74; Si 15.34, 15.31
$C_8H_{19}SiCl$. Calculated %: C 53.75; H 10.71; Cl 19.83; Si 15.69.

3-Chloro-2,2,4,4-tetramethyl-2,4-disilapentane $(CH_3)_3SiCHClSi(CH_3)_3$ (X). To CH_3MgI, prepared from 24.3 g of Mg in 400 ml of ether, 42.5 g of 1,1,1,2,3,3,3-heptachloro-1,3-disilapropane [11] was added dropwise. The ether was distilled off, and the residue was heated at about 100° for three hours. The ether was returned to the flask, and the usual treatment yielded 13 g (50%) of (X), b.p. 177-178.5°. It was not found possible to obtain (X) by the chlorination of (IV) with SO_2Cl_2, although very vigorous chlorination occurred.

Found %: Si 28.76; 28.46.
$C_7H_{19}Si_2Cl$. Calculated %: Si 28.81.

TABLE

No.	Formula of compound	Reference No.	Yield (%)	B.p. in °C (p in mm Hg)		n_D^{20}	d_4^{20}	MR Found	MR Calc'd [6]	MR Δ	MR Calc'd by us	MR Δ
1	$CH_3CH_2CH_2SiCl_3$	(I)	61.5	123.0	(747)	1.4309	1.1993	38.31	38.43	0.12	–	–
2*	$(CH_3)_2C_2H_5SiCH_2Cl$	(VI)	86	127.8	(757)	1.4295	0.8924	39.52	39.75	0.23	39.63	0.11
3*	$CH_3(C_2H_5)_2SiCH_2Cl$	(VII)	83.7	155.2	(763)	1.4402	0.9029	44.00	44.38	0.38	44.14	0.14
4	$(C_2H_5)_3SiCH_2Cl$	–	71	179.2	(743)	1.4480	0.9101	48.45	49.01	0.56	48.65	0.20
5*	$C_3H_7(CH_3)_2SiCH_2Cl$	(VIII)	55.7	151.7	(753)	1.4335	0.8891	44.18	44.38	0.20	–	–
6*	$(C_3H_7)_2CH_3SiCH_2Cl$	(IX)	70	192.0	(750)	1.4450	0.8902	53.44	53.64	0.20	–	–
7*	$(CH_3)_3SiCHSi(CH_3)_3$	(X)	50	178.5	(747)	1.4489	0.8900	58.70	58.64	0.06	–	–
8*	$(C_2H_5)_3SiCH_2\overset{Cl}{CH}CH=CHCH_3$	(XI)	73.9	214.5	(745)	1.4502	0.8016	66.54	66.85	0.31	66.49	0.05
9*	$C_2H_5(CH_3)_2SiCH_2\overset{CH_3}{CH_2}CH=CH_2$	(XII)	77.5	140 - 141	(756)	1.4257	0.7550	48.22	48.33	0.11	48.21	0.01
10*	$(C_2H_5)_2CH_3SiCH_2CH_2CH=CH_2$	(XIII)	68	166.3	(736)	1.4364	0.7743	52.82	52.96	0.14	52.72	0.10
11*	$(C_2H_5)_3SiCH_2CH_2CH=CH_2$	(XIV)	71	189.5	(755)	1.4437	0.7918	57.22	57.59	0.37	57.23	0.01
12*	$(C_2H_5)_3SiCHCH_2CH=CH_2$	(XV)	28	207.5	(755)	1.4522	0.8108	61.36	61.85	0.49	61.49	0.13
13*	$(CH_3)_3SiCH_2CH_2\overset{CH_3}{C}=CH_2$	(XVI)	51.5	134.6	(750)	1.4235	0.7541	48.10	48.33	0.23	–	–
14*	$(CH_3)_3SiCH_2CH_2\overset{CH_3}{CH_2}CH_2CH=CH_2$	(XVIII)	41.5	158 - 159	(750)	1.4246	0.7566	52.78	52.96	0.18	–	–
15*	$(C_2H_5)_3Si\underset{CH_3}{CH}-\underset{CH_3}{CH}Si(C_2H_5)_3$	(XVII)	15	294 - 297	(750)	1.4752	0.8573	94.15	95.47	1.32	94.75	0.60
15	$(C_2H_5)_3SiCH=CH_2$	–	–	146.5	(745)	1.4345	0.7728	47.99	48.33	0.34	47.97	0.02

* This compound has been prepared for the first time.

Triethyl(2-methyl-3-pentenyl)silane $(C_2H_5)_3SiCH_2\underset{CH_3}{CH}CH=CHCH_3$ (XI). A mixture of 45 g of (4-bromo-2-methylpentyl)triethylsilane [2] and 90 g of 30% ethanolic KOH was placed in an autoclave. The autoclave was rotated and heated at 170-180° for ten hours. The contents were poured into water. Fractionation of the organic layer yielded 22 g of (XI), b.p. 214.5°/745 mm, the yield being 73.9% on the amount of the 4-bromo compound that reacted. The spectra, which were determined by Yu. P. Egorov, indicated the absence of 4-alkenylsilane and showed that cis and trans isomers were present.

3-Butenylethyldimethylsilane $CH_2{=}CHCH_2CH_2SiC_2H_5(CH_3)_2$ (XII). Allyl bromide (60 g, i.e. an excess so as to deal with any excess of magnesium) was added to a cooled Grignard reagent prepared from 10.7 g of Mg and 56.5 g of (VI) in 250 ml of ether. The contents of the flask were set aside overnight, and on the next day, the ether was distilled off. It was found that distillation of the ether immediately after the addition of C_3H_5Br sometimes results in the ejection of the contents of the flask, but this does not occur when the mixture is left overnight so that the greater part of the C_3H_5Br has reacted. The solid residue was heated in a boiling water bath for five hours. The usual treatment and distillation through a sodium column yielded 45.4 g (77.5%) of (XII), b.p. 140-141°.

Found %: C 68.05; 68.05; H 12.96; 12.88; Si 19.52; 19.68
$C_8H_{18}Si$. Calculated %: C 67.53; H 12.75; Si 19.72

The other 3-butenylsilanes were obtained in a similar way.

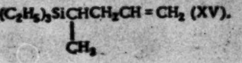
3-Butenyldiethylmethylsilane $CH_2{=}CHCH_2CH_2Si(C_2H_5)_2CH_3$ (XIII). To RMgX, prepared in 500 ml of ether from 12 g of Mg and 75 g of (VII), 70 g of C_3H_5Br was added. The contents of the flask were set aside over night and were then boiled, without removal of ether, for three hours. The product was 49 g (68%) of (XIII), b.p. 165-167°.

Found %: C 69.83; 69.54; H 13.23; 13.08; Si 17.68; 17.47
$C_9H_{20}Si$. Calculated %: C 69.15 H 12.89; Si 17.95

3-Butenyltriethylsilane $CH_2{=}CHCH_2CH_2Si(C_2H_5)_3$ (XIV). To RMgX, prepared in 250 ml of ether from 6.7 g of Mg and 45 g of (chloromethyl)triethylsilane [5], 50 g of C_3H_5Br was added. On the next day the ether was distilled off and the residue was heated at about 100° for five hours. The product was 33 g (71%) of (XIV), b.p. 188-190°.

Found %: C 70.17; 70.29; H 12.85; 12.95; Si 15.98; 15.92
$C_{10}H_{22}Si$. Calculated %: C 70.51; H 13.02 Si 16.47

Triethyl(1-methyl-3-butenyl)silane



$$(C_2H_5)_3Si\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH{=}CH_2$$

(XV). (1-Chloroethyl)triethylsilane [5] (523 g) was added slowly to 11 g of Mg in 300 ml of ether. To this Grignard reagent, 35.4 g of C_3H_5Br was added. The ether was driven off, and the residue was heated at about 100° for five hours. The product was 15 g (28%) of (XV), b.p. 206-208°.

Found %: C 70.85; 71.04; H 12.94; 12.95; Si 14.52; 14.80
$C_{11}H_{24}Si$. Calculated %: C 71.66; H 13.12 Si 15.22

There was a heavy residue of 8 ml. This was insoluble in concentrated H_2SO_4 [see (XVII)].

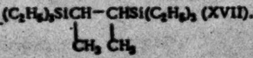
Trimethyl (3-methyl-3-butenyl)silane

$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_2CH_2Si(CH_3)_3$$

(XVI) 2-Methylallyl chloride (40 g) was added to RMgX prepared from 7 g of Mg and 36 g of (V) in 250 ml of ether. The ether was removed, and the residue was heated at about 100° for about six hours. The product was 21.5 g (51.5%) of (XVI), b.p. 134-134.6°.

Found %: Si 19.47; 19.42
$C_8H_{18}Si$. Calculated %: Si 19.72.

3,3,6,6-Tetraethyl-4,5-dimethyl-3,6-disilaoctane



$$(C_2H_5)_3Si\underset{\displaystyle CH_3}{\underset{|}{C}}H-\underset{\displaystyle CH_3}{\underset{|}{C}}HSi(C_2H_5)_3$$

(XVII). (1-Chloroethyl)-triethylsilane (59 g) was added to 8 g of Mg over a period of 40 minutes. Reaction with Mg was initiated by addition of 1 ml of C_2H_5Br. A white precipitate formed during the preparation of RMgX. The ether was removed, and the residue was heated at about 100° for two hours. The complex was decomposed with water, the ether was removed, and the residue was treated with H_2SO_4. The sulfuric acid layer was poured into water, and 15 g of hexaethyldisiloxane separated. The portion insoluble in sulfuric acid (29 g) consisted of 19.2 g (40%) of tetraethylsilane and 7.1 g (15%) of (XVII), b.p. 293-298°.

Found %: C 67.44; 67.61; H 13.24; 13.37; Si 19.23; 19.59

$C_{16}H_{38}Si_2$. Calculated %: C 67.05; H 13.36 Si 19.58

5-Hexenyltrimethylsilane $CH_2{=}CHCH_2CH_2CH_2CH_2Si(CH_3)_3$ (XVIII). To the Grignard reagent prepared from 2.5 g of Mg and 19.6 g of (3-bromopropyl) trimethylsilane [8], 26 g of C_3H_5Br was added. The ether was distilled off, and the residue was heated at about 100° for 17 hours. The product was 6.5 g (41.5%) of (XVIII), b.p. 157-160°.

Found %: C 68.13; 68.36; H 12.91; 12.95; Si 18.30; 17.67

$C_9H_{20}Si$. Calculated %: C 69.15; H 12.90; Si 17.95

SUMMARY

1. The direction of the addition of HBr to 4-alkenylsilanes has been established, and at the same time a new method has been found for the preparation of 3-alkenylsilanes by the dehydrobromination of trialkyl(4-bromoalkyl)silanes with alkali.

2. By this method, and also by the reaction of Grignard reagents prepared from trialkyl(1-chloroalkyl) silanes with allyl bromide and with 2-methylallyl chloride, six new 3-alkenylsilanes have been prepared.

3. The first 5-alkenylsilane has been prepared.

LITERATURE CITED

[1] F. C. Whitmore, Chem. Eng. News 26, No. 10, 668 (1948); A. D. Petrov and V. F. Mironov, Proc. Acad. Sci. USSR, 80, No. 5, 761 (1951); E. Larsson, Trans. Chalmer. Univ. Technol. No. 115, 23 (1951); C. A. 47, 10470 (1953); G. H. Wagner, D. L. Bailey, A. N. Pines, M. L. Dunham, D. B. McIntire, Ind. Eng. Chem. 45, No. 2, 367 (1953). L. H. Sommer, D. L. Bailey, G. M. Goldberg, C. E. Buck, J. Am. Chem. Soc., 76, 1613 (1954).

[2] A. D. Petrov and V. F. Mironov, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. 1952, No. 4, 635. *

[3] L. H. Sommer, L. J. Tyler, F. C. Whitmore, J. Am. Chem. Soc., 70, 2872 (1948).

[4] A. D. Petrov and G. I. Nikishin, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. 1952, No. 6, 1128.**

[5] V. A. Ponomarenko and V. F. Mironov, Proc. Acad. Sci. U.S.S.R., 94, 485 (1954).

[6] E. L. Warrick, J. Am. Chem. Soc. 68, 2455 (1946).

[7] F. C. Whitmore, J. Am. Chem. Soc. 68, 475 (1946).

[8] L. H. Sommer, R. E. Van Strien, F. C. Whitmore, J. Am. Chem. Soc. 71, 3056 (1949).

[9] L. H. Sommer, E. Dorfman, G. M. Goldberg, F. C. Whitmore, J. Am. Chem. Soc. 68, 488 (1946).

[10] A. V. Topchiev, N. S. Nametkin, and A. A. Shcherbakova, Proc. Acad. Sci. U.S.S.R., 86, 559 (1952).

[11] A. D. Petrov, V. F. Mironov, V. A. Ponomarenko, and E. A. Chernyshev, Proc. Acad. Sci. U.S.S.R. 97, No. 4, 687 (1954).

Received July 19, 1954

N. D. Zelinsky Institute of Organic
Chemistry of the U.S.S.R. Academy of Sciences

---

* See Consultants Bureau Translation, page 591.
** " " " " 989.

SYNTHESIS OF SODIUM TETRAPHENYLBORON

A. N. Nesmeyanov and V. A. Sazonova

It is well known that sodium tetraphenylboron [1] is of interest in analytical chemistry as a reagent for the potassium ion. In this short paper we describe a more convenient method for the preparation of sodium tetraphenylboron. In a previous paper [2] we have described the reaction of phenylmagnesinm bromide with potassium fluoborate, which leads to the formation of potassium tetraphenylboron. Sodium fluoborate reacts similarly with the organomagnesium compound:

$$NaBF_4 + 4C_6H_5MgBr \longrightarrow NaB(C_6H_5)_4 + 4MgBrF.$$

This reaction gives a 62 - 68% yield of sodium tetraphenylboron.

EXPERIMENTAL

Sodium fluoborate (6 g) was added to an ether solution of phenylmagnesium bromide, prepared from 7 g of magnesium, 46 g of bromobenzene, and 150 ml of absolute ether. The reaction mixture was stirred for 1.5-2 hours, and was then poured into water, or, preferably, saturated NaCl solution. The ether layer was separated, and the aqueous part was extracted twice with ether. The ether extracts were united, and the ether was removed under reduced pressure. The residue crystallized; it was dried, and washed free from biphenyl by means of chloroform. The product was 12.5 g of a crystalline substance containing 96% of $NaB(C_6H_5)_4$.

For purification the substance was dissolved at 0° in ether (freed from alcohol and dried over $CaCl_2$) to which 1-2 drops of water had been added [$NaB(C_6H_5)_4$ is poorly soluble in absolute ether].

The ether solution was filtered, and heated to the boil. A crystalline precipitate of sodium tetraphenylboron then formed. It was filtered off and vacuum-dried.

Found %: Na 6.70; 6.53

$C_{24}H_{20}BNa$. Calculated %: Na 6.72

A filtered aqueous solutionof 0.6 g of the preparation was added to an aqueous solution of 0.0745 g of KCl at 50°. The precipitated $KB(C_6H_5)_4$ was filtered off (through a No. 3 or No. 4 crucible), washed with water, and dried. The amount of $KB(C_6H_5)_4$ obtained was 0.3576 g, and the calculated amount was 0.3578 g.

LITERATURE CITED

[1] G. Wittig, P. Raff, Ann. 573, 195 (1951); A. F. Ievinsh and E. Yu. Gudriniette. J. Anal. Chem. 9, 270 (1954). *

[2] A. N Nesmeyanov, V. A. Sazonova, G. S. Liberman, and L. I. Emelyanova, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. 1953, No. 1, 48.**

Received November 3, 1954

M. V. Lomonosov Moscow State University

---

* See Consultants Bureau Translation, page 301.

** " " " " 43.

CURRENT EVENTS

AT THE DIVISION OF CHEMICAL SCIENCE OF THE ACADEMY OF SCIENCES OF THE USSR

A general meeting of the Division of Chemical Science of the Academy of Sciences of the USSR took place on October 21 and 22, 1954, under the chairmanship of the Academician-Secretary of the Division, Academician M. M. Dubinin. It was devoted to the reading of papers by Academician A. E. Arbuzov — on the problem of the synthesis of insecticides — by Academician S. I. Volfkovich — on a new technical process for the manufacture of fertilizers — and by the chief editor of the abstract journal "Chemistry", V. V. Serpinsky, who presented a report in connection with the first anniversary of the issue of the journal.

Academician A. E. Arbuzov discussed the investigations carried out by him and his students at the Kazan Affiliated Institute of the Academy of Sciences of the USSR on the synthesis of new organophosphorus compounds having practical importance as insecticides.

Matters relating to the structure of organic derivatives of phosphorous acid have occupied A. E. Arbuzov since 1903. One of A. E. Arbuzov's most important discoveries is the isomerization of full esters of this acid into esters of alkylphosphonic acids. This reaction, which has been given the name of "the Arbuzov rearrangement", has been studied by many chemists, here and abroad, and more than 300 examples of this rearrangement have now been investigated.* As a result of investigations by A. E. and B. A. Arbuzov from 1928 onwards on compounds derived from or related to phosphorous acid, a new and extremely simple method has been found for the preparation of free radicals of the triarylmethyl series. In the course of the investigation of the mechanism of the new reaction, esters of hypophosphoric and pyrophosphorous acids were prepared for the first time. By the addition of one or two atoms of sulfur to these compounds, new classes of organophosphorus compounds were obtained, and these were shown later to be very powerful insecticides. Of the many hundreds of these compounds that have been synthesized in recent years, particular interest is presented by tetraethyl pyrophosphate (TEPF), tetraethyl dithiopyrophosphate ("Dithio"), tetraethyl monothiopyrophosphate ("Pyrophos"), and octamethyl tetraamidopyrophosphate ("Octamethyl"). In the course of the study of these compounds, the methods for their synthesis have been simplified. Great interest has been shown recently in "Octamethyl", an insecticide having a so-called systemic action.

Academician S. I. Volfkovich discussed a new method of preparing phosphorus fertilizers and feeding stuffs for livestock by the treatment of natural phosphates (apatite and phosphorites) with steam at high temperature in presence of small amounts of mineral additives. In this hydrothermal process apatite is broken down with evolution of gaseous fluorine, and a form of phosphate that is readily assimilated by plants is formed.

Until now, the most widely used methods of manufacture have been based on the treatment of natural phosphates with acids; some electrothermal and "alkalithermal" methods have been used on a small scale. The method studied by the speaker in conjunction with workers from the Fertilizer and Insectofungicide Institute and the Chemical Technology Department of the Moscow State University does not require acids, alkalis, or electrical energy in appreciable amount, but requires only the usual fuels (fuel oil, natural gas, or coal).

Laboratory and pilot experiments have shown that a dry, free-running product containing 32-36% of citric-soluble phosphoric oxide and not more than 0.1% of fluorine (larger amounts are harmful to many animals) can be obtained by this method. The new fertilizer is about twice as rich in phosphorus as superphosphate and Thomas slag, and it is of great interest in relation to the soils of the northern belt of the Soviet Union.

The work was carried out by S. I. Volfkovich together with N. N. Postnikov, V. V. Illarionov, R. E. Remen, A. A. Ionass, N. D. Talanov, and others.

In his paper, the chief editor of the abstract journal "Chemistry" V. V. Serpinsky emphasized the important part played in the organization and publication of the journal by its first editor, B. N. Rutovsky, who had recently died. He discussed the present state of the publication of the journal and the prospects for its further improvement in the future.

The speaker emphasized the exceptional significance for chemists of the publication of an abstract journal in view of the enormous scale on which the publication of periodical literature on chemistry and related sciences was proceeding throughout the world. The total number of journals from which the material for the new abstract journal was gathered was approximately 5,500. The speaker stated that chemical abstracting has a long history, and he referred to "Chemisches Zentralblatt", which had its 125th anniversary in 1954, "Chemical Abstracts" which has been published since 1907, and a number of other abstract journals in English, French, Czech, Japanese, Spanish (published in Mexico), Rumanian, Hungarian, and other languages. Also, as is well known, numerous abstract journals are published for separate branches of chemical technology (rubber, plastics, leather, sugar, acids, and so on).

The organization of an Institute of Scientific Information within the system of the Academy of Sciences of the USSR with the function, among others, of publishing journals has provided investigators with an abstract journal in Russian, which has made it much easier for Soviet scientists, technologists, and teachers to follow the development of many branches of world science; for the Soviet abstract journal is published in numerous series — chemistry, physics, mathematics, astronomy, geodesy, mechanics, geography, geology, biology — and a new series on biochemistry is being prepared. This, the speaker pointed out, is the fundamental difference between the Soviet journal and other abstract journals. This enormous venture has been associated with the overcoming of considerable difficulties. Every day in the editorial department, the registration, examination, and marking of thousands of different journals are proceeding, and at the same time hundreds of abstracts are being written, edited, printed, and corrected. There are still further incidental difficulties, especially with respect to the translation of certain scientific and technical terms into Russian.

An important object, which has not yet been reached, is the attainment by the journal of what the speaker called "a stationary state", in which the journal will be able to print as much material as it obtains. When this has been achieved (partly by increase in volume), there will be a planned reduction in the time between the appearance of the original paper and the appearance of the abstract of that paper. It is then proposed to narrow the scope of the material to be printed in the journal "Chemistry". For example, matters concerning the atomic nucleus, the physical properties of solids, and some other subjects, will be found only in the journal "Physics". Certain mineralogical matters will be found in the journal "Geology and Geography". The possibility cannot be excluded of the occurrence of duplication of material, and, within limits, this is inevitable, for the chemist rightly expects that a single abstract journal will cover all of the subjects that interest him. One problem, the satisfactory solution of which would greatly facilitate the use of the journal, is correct rubrication. The editorial board hopes to improve it somewhat, but cannot envisage any fundamental changes. For example, the section on natural substances will be headed "Natural Substances and Steroids".

The question arises of the need for critical appraisal in an abstract. Should there be any departure from the principle of the exclusion of critical appraisal of any sort relating to the paper being abstracted? The speaker pointed out that 100% objective abstracting was impossible, but the number of editorial comments had been insignificant (only 24 for 51,000 abstracts).

In the discussion on V. V. Serpinsky's paper, the importance of the founding of the Institute of Scientific Information within the system of the Academy of Sciences of the USSR was emphasized. The significance of the new abstract journals was also stressed, and its defects were discussed.

Corr. Member B. V. Nekrasov suggested that the lengths of the abstracts should be reduced and smaller type should be used so that a fuller coverage of material could be attained.

Prof. G. B. Boky considered that one of the defects was the nonuniformity of terms and symbols in the abstract journals of different series — "Physics" and "Chemistry", for example. Prof. G. B. Boky recommended that the Institute of Scientific Information should take an active part in the development of chemical nomenclature.

Corr. Member A. F. Kapustinsky stressed the need for an objective presentation of the contents of the papers, without any critical remarks or reservations. He considered that the section on geochemistry in the journal "Chemistry" should be extended.

Academician A. N. Frumkin considered that one of the most important problems for the journal was the attainment of a stationary state with respect to world literature; also, the publishing of fuller patent information is desirable.

Corr. Member A. P. Terentyev drew attention to the need for the careful compilation of subject and formula indexes and for the systematization of chemical nomenclature.

Corr. Member Ya. I. Gerasimov suggested that the journal "Chemistry" should be issued in the form of separate sections in order to make it less costly to the reader and less bulky when kept in annual sets.

G. V. Bykov, Cand. Chem. Sci., considered that books should be reviewed and not simply listed bibliographically. He suggested also that abstracts should be given of papers on the history of chemistry.

V. I. Kuznetsov, Doc. Chem. Sci., and others recommended that abstracts should be made of theses, which are generally difficult of access to the reader.

Among those who discussed the need for paying great attention to the abstracting of patents were Corr. Member M. I. Kabachnik, Corr. Member A. V. Novoselova, A. I. Korolev, Doc.Chem.Sci., and N. N. Vorozhtsov.

At the same time the poor coverage of technological chemistry in the journal was pointed out.

The chairman, Academician M. M. Dubinin, in summing up the discussion, particularly stressed the importance of the widest possible participation of chemists in the work of the journal. Without this, improvements cannot be effected, and this is especially true of the abstracting of scientific papers and patents in the important section of chemical technology. The Editorial Board should seek the cooperation of the active members of the Mendeleev All-Union Chemical Society and the Ministry of Chemical Industry, and they should convene a special conference on this subject. Academician M. M. Dubinin made a number of concrete suggestions relating to the increasing of the responsibility of the institutes of the Division of Chemical Science of the Academy of Sciences of the USSR for the high quality of the material in the journal.

The chief editor of the journal V. V. Serpinsky agreeed with most of the remarks that had been made, and he stated that one of the most serious defects of the journal was the inadequate development of the technological section. Measures would be taken in the near future for the removal of this defect. The Editorial Board would like to see reviews of the abstract journal "Chemistry" in the periodical press.

BLANK
PAGE

Field of Solid Solutions formed by Celsian, Dibarium Trisilicate and Barium Disilate. p. 1

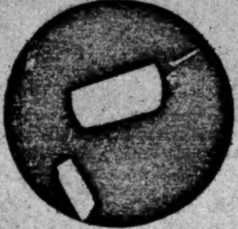


Fig. 3. Crystals of barium disilicate (3% Al_2O_3, 1250°, crossed nicols).

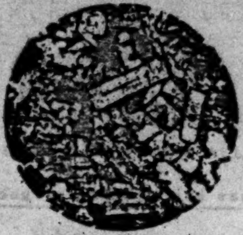


Fig. 4. Crystals of solid solution, (9% Al_2O_3, 1340°, crossed nicols).

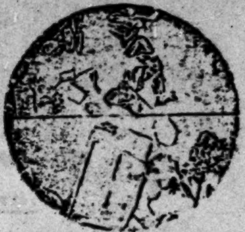


Fig. 5. Crystals of solid solution, (3% Al_2O_3, 1270°).

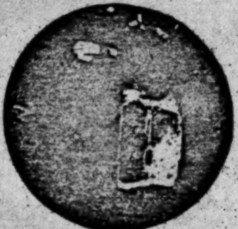


Fig. 6. Crystals of solid solution (3% Al_2O_3, 1270°, crossed nicols).

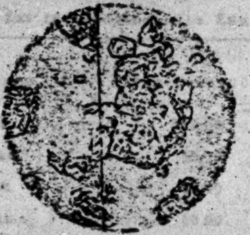


Fig. 7. Crystals of solid solution (6% Al_2O_3, 1200°.

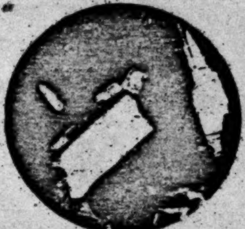


Fig. 8. Crystals of solid solution, (6% Al_2O_3, 1240°, crossed nicols).

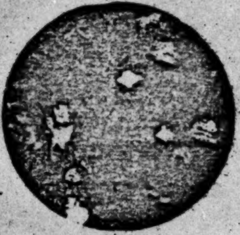


Fig. 9. Crystals of solid solution and celsian (9% Al_2O_3, 1200°, crossed nicols).

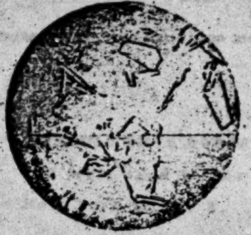


Fig. 10. Crystals of solid solution and barium metasilicate (1250°).

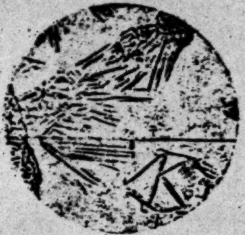


Fig. 11. Crystals of celsian (1380°)

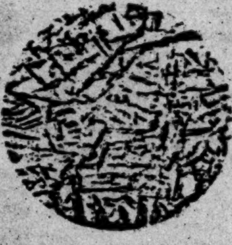


Fig. 11. Crystals of solid solution and celsian (taken by reflected light)

Babinet's Principle, and the Low-Angle Scattering of X-rays by Porous Glasses. p. 19

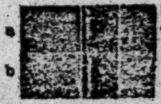


Fig. 1. X-Ray pictures: a) original specimen of highly dispersed porous glass; b) the same glass treated with KOH for (2 + 2) hours. The light band is the trace of the trap for the primary beam. The minimum scattering angle is 6,5', and themaximum is about 1,5°.

TRANSLATION TO AND FROM ALL LANGUAGES

by bilingual chemists and engineers:

Rates for translation into English

Language	Price per 1000 words
French	$10.00
German	10.00
Italian	10.00
Russian	10.00
Spanish	10.00
Dutch	12.00
Other languages	Rates upon request

CONSULTANTS BUREAU
152 West 42nd Street
New York 18, N. Y.

CRYSTAL-OPTICAL METHOD FOR DETERMINING THE STRUCTURES OF COMPLEX COMPOUNDS

G. B. Boky and S. S. Batsanov

In recent years, in the Department of Crystallography and Crystal Chemistry of the Moscow State University and in the Crystal Chemistry Laboratory of the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR, a new crystal-optical method has been developed for determining the structures of complex compounds [1, 2, 3]. By this method the geometric configuration, and sometimes also the interatomic distances in the inner sphere of the complex compound, can be determined with adequate accuracy.

The determination of the geometric configuration is based essentially on a comparison of the experimentally measured refractive indices with the theoretically calculated values (from the component refractions) for the various isomeric forms. The refractive indices are calculated from the Lorentz-Lorenz formula, which is solved for n^2. Hence, for the calculation of the refractive indices of complex compounds, the component refractions must be known.

The molar refractions of ionic compounds in the crystalline state can, to a first approximation, be compounded additively from the ionic "crystal" refractions, as we have shown in previous papers [1, 3]. Hence, for the calculation of the refractions of ionic complex compounds, it is sufficient to know the refractions of the corresponding ions.

The refractions of cations have been determined by Fajans [4] for the gaseous state. Since variations in the refractions of cations due to changes in polarization conditions can be neglected, Fajan's values can be used directly for the calculation of the molar refractions of solid salts, including salts having complex anions. The refractions of simple anions are given for the crystalline state in our previous papers, cited above, where they were determined from data for crystals of alkali-metal salts. The refractions of complex ions can be calculated from coordinate refractions [5]: thus the refraction of the ion $[PtX_6]$ is three times that of the X − Pt − X coordinate, the refraction of the ion $[PtX_5Y]$ is the sum of two X − P − X refractions and one X − Pt − Y refraction, and so on. The coordinate refractions for bi-, and quadri-valent platinum and tervalent cobalt compounds have already been published by us [6], and the experimental data from which the coordinate refractions of quadrivalent platinum were calculated are given in the present paper. It must be pointed out that the Lorentz-Lorenz formula by which the refractions were calculated is strictly applicable only to isotropic media and to refractive indices extrapolated to infinite wavelength. Since the crystals of almost all of the compounds considered in this paper are optically anisotropic, the value of refractive index that we have substituted in the formula is averaged by the formula $n = {}^{3}\, n_g \cdot n_m \cdot n_p$ and is extrapolated to infinite wavelength with the aid of the dispersion measurements.

The present paper is concerned with the determination of the geometric configuration of complex compounds of quadrivalent platinum. We have measured the dispersion of the refractive indices for several quadrivalent platinum complex compounds and calculated the refractive indices for infinite wavelength. The densities of most of the compounds were measured in M. M. Yakshin's laboratory, and we determined some of them ourselves by means of a pyknometer.

Table 1 gives the data on the dispersion of the refractive indices of quadrivalent platinum compounds. The extrapolation was carried out graphically by Wulf's method [7].

From the experimental data we calculated the coordinate refractions for quadrivalent platinum compounds. In these calculations we used our previously published ionic refractions [3] and the refraction for crystallization water as determined by Batsanov [8]. In the calculation of the refraction of the coordinate $NH_3 - Pt - NO_2$ from the data for dichlorodinitroammineplatinum, account was taken of the formation of a hydrogen bond NH...O (between oxygen of the nitro group and hydrogen of ammonia) by making the necessary correction (0.38 cc) [8].

From the data in Table 2 the geometric configurations of a group of chloroammine and chloronitro quadrivalent platinum compounds can be determined. Results of these calculations are given in Table 3.

It will be seen from Table 3 that the square of the refractive index calculated for the actual structure of the

TABLE 1

Formula of compound	λ	486	520	555	589	620.	656	∞
$(NH_4)_2PtCl_6$	n_m	1.878	1.863	1.853	1.843	1.836	1.830	1.713
$Pt(NH_3)_2Cl_4$ cis	n_g	2,040	2,020	2,006	1.994	1.985	1.977	1.820
	n_m	1.909	1.893	1.882	1.870	1.863	1.855	1.716
	n_p	1.877	1.862	1.852	1.842	1.835	1.829	1.712
$Pt(NH_3)_2Cl_4$ trans	n_g	2,047	2,027	2,013	2,002	1.992	1.984	1.826
	n_m	1.889	1.878	1.867	1.856	1.849	1.843	1.717
$[Pt(NH_3)_3Cl \cdot H_2O$ trans	n_g	1.909	1.893	1.882	1.870	1.863	1.855	1.716
	n_m	1.806	1.792	1.782	1.772	1.766	1.761	1,654
	n_p	1.720	1.709	1.701	1.694	1.689	1.684	1,593
$[Pt(NH_3)_4Cl_2]\ Cl_2$ trans	n_g	2,042	2,022	2,008	1.996	1.987	1.979	1.821
	n_m	1.773	1.761	1.753	1.745	1.739	1.735	1,635
$Pt(NH_3NO_2)_2Cl_2$	n_m	1.815	1.803	1.793	1.784	1.777	1.771	1,655
$K_2Pt(NO_2)_3Cl_3$ cis	n_g	1.918	1.902	1.891	1.879	1.872	1.864	1.728
	n_m	1.822	1.809	1.800	1.791	1.784	1.779	1,666
	n_p	1.768	1.756	1.748	1.740	1.734	1.729	1,628
$K_2Pt(NO_2)_3Cl_3$ trans	n_g	1.822	1.809	1.800	1.791	1.784	1.779	1,666
	n_m	1.792	1.778	1.769	1.761	1.755	1.750	1,645
	n_p	1.749	1.737	1.728	1.720	1.715	1.711	1,609
$K_2Pt(NO_2)_4Cl_2$ cis	n_g	1.844	1.830	1.820	1.210	1.803	1.797	1,676
	n_m	1.787	1.773	1.764	1.756	1.750	1.745	1,640
	n_p	1.753	1.741	1.732	1.724	1.719	1.715	1,613
$K_2Pt(NO_2)_4Cl_2$ trans	n_g	1.813	1.800	1.790	1.780	1.774	1.763	1,651
	n_m	1.757	1.746	1.738	1.730	1.724_5	1.720	1,618
	n_p	1.741	1.731	1.723	1.716	1.711	1.706	1,614

TABLE 2

Coordinate	Compound	M	d	π_{∞}	$R^{\infty}_{\text{com-d}}$	$R^{\infty}_{\text{coord}}$	
Cl – Pt – Cl	K_2PtCl_6	486.16	3.474	1.722_5	55.42	16.97	16.90
	$(NH_4)_2PtCl_6$	444.05	3.065	1.713	56.79	16.84	
Cl – Pt – NH_3	$Pt(NH_3)_2PtCl_6$ cis	371.06	3.420	1.759	44.20	13.65	
NH_3 – Pt – NH_3	$[Pt(NH_3)_4Cl_2]Cl_2$ trans	405.18	2.927	1.695	53.21	9.83	
NH_3 – Pt – NO_2	$Pt(NH_3NO_2)_2Cl_2$	392.14	3.040	1.655	45.86	14.29	
NO_2 – Pt – NO_2	$K_2Pt(NO_2)_4Cl_2$ trans	528.37	3.140*	1.628	59.72	19.16	
NO_2 – Pt – Cl	$K_2Pt(NO_2)_4Cl_2$ cis	528.37	3.156*	1.643	60.54	18.44	18.50
	$K_2Pt(NO_2)_3Cl_3$ cis	517.82	3.226	1.673	60.17	18.56	

*Measured by us.

TABLE 3

Formula of compound	M	d	$\bar{n}^2_{opt}$	R_∞	$\bar{n}^2_{calc}$	Δn^2_∞
$Pt(NH_3)_2Cl_4$ trans	371.08	3.508	3.071	cis 44.16	3.150	0.079
				trans 43.63	3.106	0.035
$[Pt(NH_3)_4Cl_2]Cl_2$ trans	405.18	2.927	2.871	cis 53.71	2.902	0.031
				trans 53.19	2.872	0.001
$[Pt(NH_3)_3Cl_3]Cl \cdot H_2O$ trans	406.16	2.877	2.741	cis 52.24	2.762	0.021
				trans 51.98	2.748	0.007
$K_2Pt(NO_2)_3Cl_3$ cis	517.82	3.226	2.799	cis 59.82	2.785	0.014
				trans 59.06	2.746	0.053
$K_2Pt(NO_2)_3Cl_3$ trans	517.82	3.151	2.689	cis 60.00	2.725	0.036
				trans 59.06	2.683	0.006
$K_2Pt(NO_2)_4Cl_2$ trans	528.37	3.156	2.699	cis 60.78	2.710	0.011
				trans 59.72	2.663	0.036

compound is always much closer to the experimental value than the value calculated for the isomeric structure. It follows that the geometric configurations of complex compounds of quadrivalent platinum can be determined by comparing the calculated and experimentally measured refractive indices.

The last compound listed in Table 3 was synthesized recently in A. V. Babaeva's laboratory, and the crystal-optical method has provided the first physicochemical proof of the structure of this interesting complex compound.

In conclusion we will point out the advantages of the crystal-optical method: first, there is the rapidity with which questions of structure can be resolved (the whole of the work can be done in 1-2 days); and second, there is the lack of stringent requirements with respect to the quality of the sample investigated (very small, poorly formed crystals, and also amorphous powders, can be investigated by this method).

These advantages of the refractometric method, coupled with its general suitability for the resolution of questions of structure, give us reason to hope that it will ultimately become one of the working methods of the chemistry of complex compounds. The refractometric method can be applied also in the solution of theoretical problems: thus it enables an approach to be made to the quantitative evaluation of the trans effect [6].

SUMMARY

The crystal-optical method for determining the structures of complex compounds has been extended to compounds of quadrivalent platinum. The stucture has been determined, for the first time, of a compound, $K_2Pt(NO_2)_4Cl_2$, recently synthesized by A. V. Babaeva: it has been shown to be the cis isomer.

Received April 27, 1954

N. S. Kurnakov Institute of General and Inorganic Chemistry
of the USSR Academy of Sciences

LITERATURE CITED

[1] G. B. Boky and S. S. Batsanov, Bull. Moscow State Univ., 2, 147 (1952).
[2] G. B. Boky and S. S. Batsanov, Bull. Moscow State Univ., 9, 89 (1952).
[3] G. B. Boky and S. S. Batsanov, Bull. Moscow State Univ., 10, 87 (1954).
[4] K. Fajans, Z. phys. Chem. (B) 24, 103 (1934).
[5] M. M. Yakshin, Bull. Platinum Sect., 21, 146 (1948).
[6] G. B. Boky and S. S. Batsanov, Proc. Acad. Sci. USSR, 95, No. 6, 1205 (1954).
[7] P. Wulf, Z. phys. Chem. (B) 21, 368 (1933).
[8] S. S. Batsanov, Bull. Moscow State Univ., 9, 95 (1954).

BLANK
PAGE

STRUCTURE OF SODIUM BOROSILICATE GLASSES IN ITS RELATION TO THE PHENOMENON OF OPALESCENCE

COMMUNICATION 2. INVESTIGATION OF THE STRUCTURE OF POROUS GLASSES[*]

S. P. Zhdanov, E. A. Porai-Koshits, and D. I. Levin

By the treatment of sodium borosilicate glasses of certain compositions with various acids it is possible to prepare porous glasses, the structures of which (the sizes and forms of the pores and the internal surface area) depend on the composition of the original glass, the thermal history of the glass, the concentration of the acid, the brittleness of the pieces of glass being treated, the temperature of the treatment, and so on [2, 3]. The object of the investigation described in this paper was the establishment of the relationship between the structure of a porous glass and its opalescence. The method of preparing the samples and the leaching conditions were therefore standardized as far as possible, and only the thermal treatment of the original glass was varied, this being responsible for the degree of opalescence (which was varied down to a state of complete clarity) of a glass of given composition.

EXPERIMENTAL

The structures of the porous glasses were studied by three independent methods: the adsorption method, the method based on the low-angle scattering of X-rays, and the electron-microscope method. Since the problem of investigating the structures of highly dispersed substances is very complex, the simultaneous application of several methods, each of which has specific merits and demerits, should ensure that the conclusions based on the investigation will be reliable.

1. Adsorption Method

The adsorption method for the investigation of the structures of porous substances is simple and has been used extensively [4-6]. Adsorption and desorption isotherms provide the basis for the determination of the main elements of the structures of porous adsorbents, i.e. the total volume of the pores, their surface area, and their effective radii.

The first investigations of one of the authors [3] showed that the structures of porous glasses in the state in which they are obtained after the acid treatment, as determined from vapor-adsorption isotherms, are usually independent of the opalescence properties of the original glasses. Further investigations have shown, however, that it is possible, under certain conditions, to find considerable differences in structure between porous glasses prepared from opalescent and nonopalescent glasses. These differences are observed when the porous glasses are treated with alkali, and they are found to be related to the structures of the original sodium borosilicate glasses [7]. Our previous investigations were carried out on a glass of composition Na 70 − 23[**]. In this section of the paper we are concerned with the glasses Na 75 − 20, Na 65 − 28, and Na 65 − 30.

By holding the glasses at temperatures of 650° and 725°, we obtained opalescent and nonopalescent samples, respectively. The porous glasses were prepared by treatment of glass powder in 3 N HCl at 50°.[***] For all of the samples of porous glass, the isotherms for the adsorption and desorption of methanol vapor at 15° were determined before and after treatment of the glass with 0.5 N KOH for one hour. Typical isotherms for samples prepared from opalescent and nonopalescent glasses are given in Figs. 1 and 2.

---

[*] The first communication described an investigation by the authors of the opalescence of sodium borosilicate glasses [1].

[**] The first figure denotes the mole percentage of silica and the second that of boric anhydride; the remainder is sodium oxide.

[***] To denote porous glasses obtained from glasses of various compositions quenched from different temperatures we shall write expressions such as $[\mathrm{Na}\ 70-23]_{725^\circ}$, in which the subscript is the temperature from which the original glass was quenched.

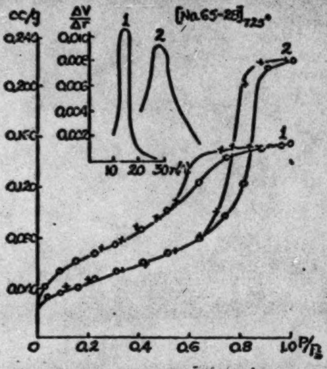


Fig. 1. Methanol adsorption isotherms before (Curve 1) and after (Curve 2) treatment of the glass with alkali.

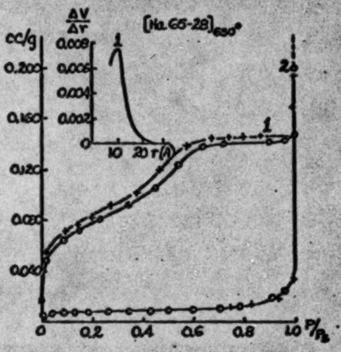


Fig. 2. Methanol adsorption isotherms before (Curve 1) and after (Curve 2) treatment of the glass with alkali.

Table 1 gives values, calculated from the isotherms, for the total volume of pores, their surface, and their most probable radius for all of the glasses investigated, before and after the alkali treatment.

From Figs. 1 and 2 and Table 1 it can be seen that treatment of porous glasses with 0.5 N KOH always increases the total volume of pores and their radii, but results in a reduction in adsorptive power at low relative pressures, and therefore in a reduction in surface area. It will be immediately obvious that porous glasses prepared from opalescent and nonopalescent glasses of the same composition yield products differing greatly in properties and in strucutre.

TABLE 1

Composition of original glass	State of original glass	Before alkali treatment			After alkali treatment		
		total volume of pores (cm^3/g)	surface area (sq. m/g)	predominant pore radius (A)	total volume of pores (cm^3/g)	surface area (sq. m/g)	predominant pore radius (A)
NA 75 − 20	Nonopalescent	0.143	260	13	0.166	228	20
	Opalescent	0.109	213	10	0.348*	38	~300
Na 65 − 28	Nonopalescent	0.153	198	15	0.220	140	28
	Opalescent	0.146	232	11	0.200*	26	~300
Na 65 − 30	Nonopalescent	0.247	300	18	0.364	246	28
	Opalescent	0.244	280	34	0.458*	212	~300

---

* Equilibrium at $p/p_s = 1$ was established very slowly, and it is possible that in these experiments the limiting value of the sorption was not attained in 24 hours.

In the first case treatment of the porous glasses with alkali yields very coarsely porous products and results in a considerable reduction in surface area* . For these products capillary condensation begins only when p/p_s

---

*The glass [Na 65 − 30] is exceptional. It is clear that when this glass is treated with alkali the formation of the very large pores characteristic of all opalescent glasses does not prevent the retention of a considerable number of fine pores.

is close to unity, and there is no second inflexion in the curve in the region of capillary condensation. When the glass powder is washed with water after the alkali treatment, the alkali is readily removed from within the grains of the powder, and already after 2-3 hours no trace of alkali can be detected with phenolphthalein. In the second case the pore radii of porous glasses are not significantly increased and the surface area is only slightly reduced. There is a second point of inflexion on the isotherms, and the region of capillary condensation is limited by certain upper values of p/p_s that are less than unity. Alkali is removed only very slowly when the glass powder is washed with water – several days are required. It must be emphasized that, before the alkali treatment, the porous glasses that are being compared were extremely similar in properties and structure (see the 3rd, 4th and 5th columns of Table 1).

It is very difficult to interpret the results if it is assumed that the increase in the radii and total volume of the pores occuring when porous glasses are treated with alkali results from the gradual widening of the pores by the dissolution of the silica forming their walls and that the rigid skeleton of a porous glass is formed throughout by silica of constant characteristics through which the pores are distributed uniformly. The following objections can be raised to these ideas: 1) if the pores are constantly becoming wider as the silica forming their walls dissolves, their surface area should increase, and not diminish, which is what it actually does; 2) the volume of the pores does not increase in proportion to the square of the radius, but at a much lower rate; 3) no explanation is provided for the great difference between opalescent and nonopalescent glasses with respect to the solubility of the silica of the pore walls; 4) the thickness of the walls of the pores of porous glasses cannot be so great that an increase in pore radius under the action of alkali from 10 to 300 A would not result in the total destruction of the porous structure.

The experimental results are satisfactorily explained if it is assumed that porous glasses can be represented as a combination of two structures: the coarse structure of the silica skeleton, i.e. that part of the structure of the original glass which was formed mainly of silica and remained almost unchanged during the treatment with acid; and the fine secondary structure within the cells of the skeleton [3]. This secondary structure is built of finely dispersed, hydrated silicic acid; it was formed during the interaction of the sodium borosilicate glass with acid [1]. It is logical to assume that the rate of dissolution of the finely dispersed silicic acid in alkali will be much greater than that of the vitreous silica of the walls of the coarsely built skeleton. The fine structure of the pores may be completely destroyed in a short treatment with 0.5 N KOH in the cold, whereas the structure of the coarsely cellular skeleton will suffer no appreciable change during the same time. When alkali-treated porous glasses are washed with water, the reaction products that have accumulated within the cells of the skeleton will be extracted, and the resulting porous product will retain all the peculiar features attributable to the silica skeleton.

According to this view of the structure of porous glasses and the mechanism of the action of alkali, the destruction of the fine structure will be accompanied by a great increase in the radii of the pores and a reduction in pore surface as the total volume of pores increases, and this is the phenomenon that is actually observed. Hence, treatment of porous glasses with alkali lays bare the silica skeleton, which is masked in porous glasses by a fine secondary structure, and makes it accessible for investigation by adsorption methods. It is evident that this fine structure is not in any way related to the opalescence of the original glass, but the structure of the silica skeleton is closely related to the opalescence characteristics of the sodium borosilicate glass, as the results described above and previously [3, 7] show.

2. Method based on the low-angle scattering of X-rays

Investigation by the low-angle scattering of X-rays permits the detection of regions of inhomogeneity in the material under examination which have linear dimensions of 20 to 1000 A and higher. The theory of the method, the experimental technique, and the first attempts to apply it to porous glasses have already been described [8-10]. It has been established from observations on the effect of artificially widening the pores that low-angle scattering by porous glasses is almost always determined by the pores, the radii of which can be determined by analysis of the diffraction pictures [11].

In order to investigate the effect of the thermal treatment of the original sodium borosilicate glasses on the structures of the porous materials obtained from them by the action of acids, glasses of six different compositions were examined: Na 75 – 20, Na 70 – 24, Na 70 – 23; Na 65 – 30, Na 65 – 28; and Na 60 – 30. Two samples of each of these were heated for two hours at different temperatures, differing by 5-20° and chosen so that, as far as possible, the maximum opalescence would be obtained at the lower temperature, and complete clarity at the higher. The values of these temperatures, which were measured accurately within ± 3°, depended on the composition and previous thermal history of the glass. After being heated, all of the glasses were ground and treated with 3 N HCl under standard conditions. The X-ray diagram was obtained in the apparatus already described [10]*.

---

* The preparation and X-ray investigation of the specimens were carried out by the graduate student N. G. Minaev.

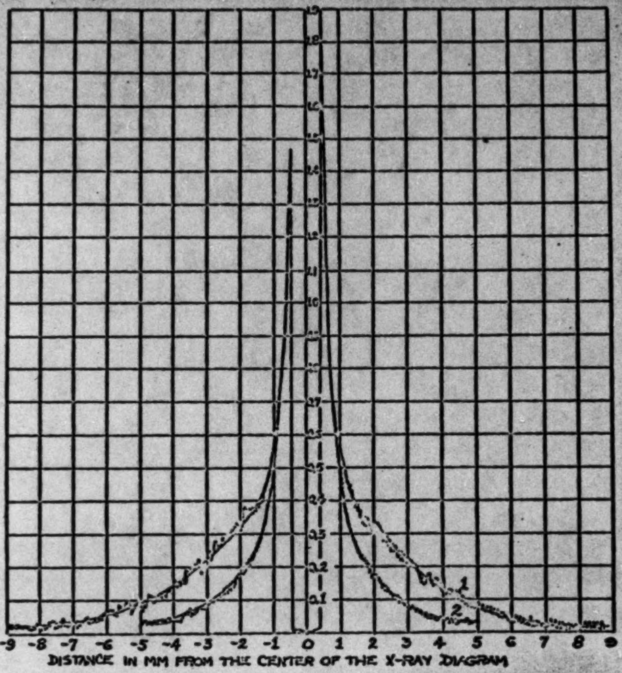


Fig. 3. Microphotometric curves for the porous glass $[\text{Na } 70 - 23]_{700^\circ}$, before (1) and after (2) its treatment with 0.5 N KOH

Fig. 3 shows the microphotometric curves for the porous glass $[\text{Na } 70 - 23]_{700^\circ}$, before and after the alkali treatment. These results differ from those of the adsorption investigation in that the coarsely porous structure — which is responsible for the intense scattering at the very lowest angles (the coincident parts of the curves) — is revealed by the X-rays not only after, but also before the alkali treatment of the porous specimen. The two curves differ only at the highest angles, i.e. in the part concerned with scattering by the highly dispersed secondary structure. Also, the removal of this highly dispersed part increases the total scattering intensity, as determined from the exposure, sometimes twenty or thirty times. This indicates a great increase in the difference between the electron densities of the walls of the basic silica skeleton and those of the channels freed from secondary silicic acid. This result provides convincing confirmation of the results of adsorption investigations [3], and it enables us to utilize the effect of alkali for the purpose of shortening the exposure, since it is the structure of the basic skeleton, not that of the secondary silicic acid, which is of interest to us in the present investigation. For this reason, before being examined by X-rays, all of the glasses were treated with alkali, washed, and dried.

The microphotometric curves for all of the samples provide an extremely clear illustration of the main result of the X-ray investigation: as the opalescence of the original glass disappears (i.e. as the temperature of treatment rises), the structure of the porous skeleton of the porous glass undergoes great changes, the large channels or cells (original glass opalescent) being replaced by finer channels (original glass clear). This can be seen, for example, when the microphotometric curves for the porous glasses $[\text{Na } 70 - 23]_{700^\circ}$ and $[\text{Na } 70 - 23]_{705^\circ}$ are compared (Fig. 4).

The sharp fall in the scattering curve for very low angles (about 10') indicates the coarsely porous structure

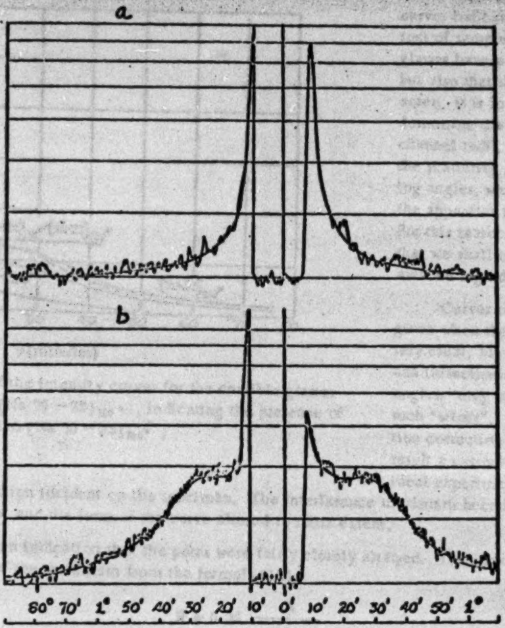


Fig. 4. Microphotometric curves for porous glasses: a) $[\mathrm{Na}\ 70-23]_{700°}$; b) $[\mathrm{Na}\ 70-23]_{705°}$

of the glass, the pores of which do not form a closely packed system; and the slower fall in this curve at angles of about 1.5° is concerned with the finely porous structure of the glass, and the presence of inflexions, or of a maximum (clearly manifest after the introduction of the collimation correction) points to fairly close packing of these pores. We may point out that this close packing is confirmed by electron micrographs (see Fig. 8), in which the walls between the fine pores are seen to be very thin.

Some of the microphotometric curves give clear indications of the presence of a dual structure in the specimens: this may be explained by inadequate thermal treatment of the original glasses, the disappearance of the opalescence and the structure associated with it being then incomplete. Other features of the curves are the rapid fall at the very lowest angles (associated with coarse pores) and "wings" (associated with fine pores). The correctness of the explanation is readily proved by a simple summation of the ordinates of the scattering curve for two extreme cases – for glass without fine pores, and for glass without coarse pores – as shown in Fig. 5 for the glass $[\mathrm{Na}\ 70-23]$ prepared from an original glass that had been cooled slowly. The summation curve (broken line) is almost coincident, within the experimental error, with the curve for the porous glass $[\mathrm{Na}\ 70-23]_{710°}$, thus showing that both structures are present in this glass.

The above discussion is illustrated in the scheme in Fig. 6, in which intensity curves of various types are given. Quantitative calculations by different methods are possible for two types of curves – those for samples containing only large pores, and those for samples containing only fine pores, i.e. samples prepared from glasses that are opalescent throughout and those prepared from glasses that are completely clear throughout, respectively.

Curves of the first type, which have no maxima or points of inflexion, can be replaced by an exponential function, or a sum of exponentials, and so do not require a collimation correction in the determination of pore radii by the "method of tangents" [3]; the collimation correction would not affect the form of the $(\log I, \nu^2)$.

graph from which the radii are determined (I is the intensity and φ is the scattering angle).

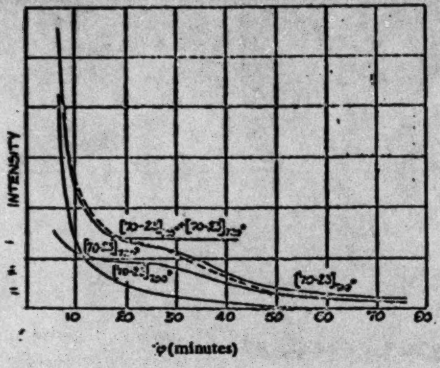


Fig. 5. Summation of the intensity curves for the crucible glasses [Na 70 − 23]$_{700°}$ and [Na 70 − 23]$_{720°}$, indicating the presence of dual structure in the glass [Na 70 − 23]$_{720°}$.

The results of calculations on such curves indicate not only that the main skeletons of samples obtained from opalescent glasses have a coarsely porous structure, but also that they have a polydisperse character; it is in fact generally impossible to determine the upper limit of the pore or channel radii, since the relevant part of the scattering curve lies at very low scattering angles, which cannot be examined with the apparatus at our disposal (less than 6'). For this reason, the mean pore dimensions that we shall cite for samples of this type must be regarded as somewhat low.

Curves of the second type, which are given when the original glasses are completely clear, always have "wings", i.e. maxima and inflections at fairly high scattering angles; they may even consist solely of such "wings". For such curves a collimation correction was introduced, and as a result a corrected curve was obtained for ideal experimental conditions — a primary X-ray beam of zero section incident on the specimen. The interference maximum became sharper and moved to higher scattering angles, and the form of the curve altered to some extent.

This was mainly an indication that the pores were fairly closely arrayed. The mean pore radius was determined from the new position of the maximum from the formula [11]:

$$R \approx 0.32 \frac{\lambda}{\varphi_{max}}$$

(λ is the wavelength of the rays used, and φ_{max} is the scattering angle at the intensity maximum.)

The values of pore radii calculated in this way were compared with those determined by the first method (method of tangents) as applied to the "tail" of the curve, i.e. the part of the curve corresponding to the highest angles (the interference maximum, while greatly affecting the central part of the curve, has little effect on its beginning and terminal parts; the method of tangents cannot, however, be applied to the beginning part of the curve, i.e., at the lowest angles, owing to the experimental inaccessibility of this part).

For all of the finely porous samples, excellent agreement was obtained between the two methods of calculation. Strictly speaking, this proves only that it is the pores of smallest radius that are closely packed, resulting in the appearance of an interference maximum. However, the absence of any appreciable scattering at the very lowest angles enables us to infer that there are no pores of greater radius in the samples, at least in the range of dimensions in which we are interested. It may be concluded, therefore, that the finely porous samples obtained from clear glasses are monodisperse.

Table 2 gives the results of the calculations for all of the investigated samples. It will be seen from these that the mean radius of the main channels of samples obtained from opalescent glasses is several times, some times more than ten times, as great as the mean radius of the main channels of samples prepared from clear glasses.

It is interesting to note that it is the glasses that were not obtained in a completely clear state (Na 70 − 24, Na 65 − 30 and Na 65 − 28) which have given products, after treatment with acid and alkali, having pores of large radius (61, 59 and 79 A respectively), as compared with those of the remaining samples. This can be ascribed to the effect of the opalescent part of the original samples. It may therefore be assumed that radii of 35-45 A are characteristic of the main channels in all porous glasses obtained from glasses that have been heat-treated at temperatures above those of the opalescence zone, i.e. that the dimensions of the regions of inhomogeneity in clear glasses of this sort are not greatly dependent on their composition.

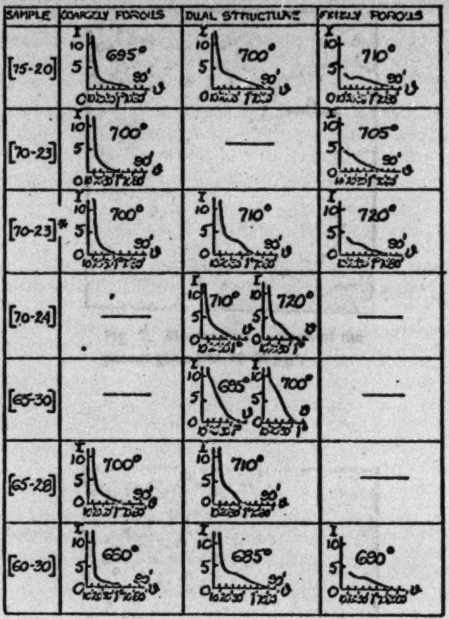


Fig. 6. Intensity curves for porous glasses.

Investigation by low-angle scattering of X-rays applied to porous glasses prepared from original glasses varying in composition and thermal history has therefore enabled us to determine the dimensions of the cells of the silica skeleton and to establish a definite relationship between these dimensions and the opalescence of the original glass. We must again emphasize that we are concerned here with the cells or channels in the silica skeleton, and not with the finer pores between the highly dispersed particles of secondary silicic acid, which may be formed, under certain conditions, within the channels of the basic skeleton.

3. Electron-microscope method**

In electron-microscope investigations of the structure of porous glasses various difficulties arise. The main difficulty is that the dimensions of the pores of porous glasses are generally beyond the limits of resolution of the microscope. Even when the pore dimensions are sufficiently great, it is still far from easy to obtain a good clear photograph: only the pores that penetrate right through the particle of porous glass and are oriented in the direction of the electron beam, i.e., perpendicular to the plane of the image, are visible on the electron micrographs.

There is frequently a gray background on the micrographs. This probably arises from the presence of very finely dispersed particles of silicic acid, which cover the collodion film as a continuous layer, so that it is not completely transparent to electrons. Finally, when porous glasses are being examined, a displacement is often observed in the image on the screen of the microscope; this is associated with the formation of a charge on the surface of the particles of the porous glass under the action of the electron beam. This displacement results in a certain diffuseness in the outlines of the particles and pores in the electron micrographs..

TABLE 2

Composition of the original glass, mole %			Original glass opalescent		Original glass clear			
			temperature of treatment of original glass (°C)	mean radius of main channels (A)	temperature of treatment of original glass (°C)	radius of main channels		
SiO_2	B_2O_3	Na_2O				from "tail of curve (A)	from position of maximum (A)	mean radius (A)
75	20	5	695	> 130	715	37	43	40
70	24	6	–	–	720	60	62	61
70	23	7	700	> 640	705	45	47	46
65	30	5	–	–	700	55	63	59
65	28	7	700	> 165	710	80	78	79
60	30	10	680	> 200	690	37	39	38

---

*Crucible glasses, i.e. glasses cooled very slowly after the fusion and therefore having an opalescent, milky appearance.

**The electron-microscope investigations were carried out with the kind cooperation of V. N. Vertsner, to whom the authors express their deep gratitude.

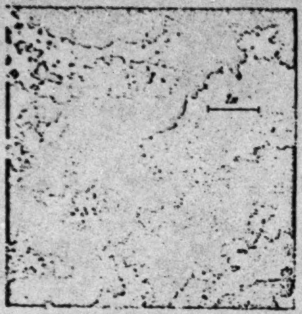


Fig 7. Electron micrograph of the porous glass [Na 70-23]$_{750°}$.

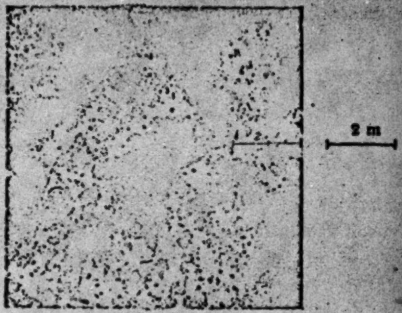


Fig. 8. Electron micrograph of the porous glass [Na 70-23]$_{550°}$ after treatment with 0.5 N·KOH

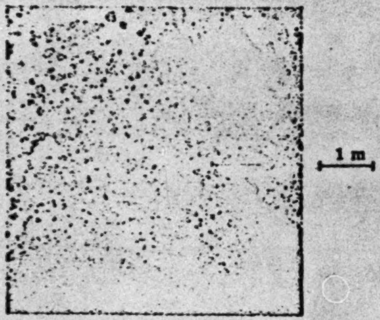


Fig. 9. Electron micrograph of the porous glass [Na 70-23]$_{650°}$. after treatment with 0.5 N KOH.

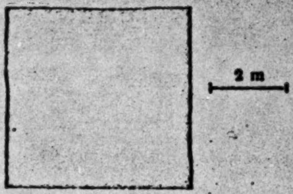


Fig. 10. Electron micrograph of the porous glass [Na 70-23]$_{700°}$.

The conditions under which the specimen is prepared, particularly the degree of grinding, must be selected with due regard for the characteristics of the porous structure of the sample under investigation. When suitable conditions are selected, it is possible to obtain micrographs which reveal the peculiar features of the structure and which enable an estimate to be made of the pore radii of porous glasses. Specimens were prepared for investigation under the electron microscope by applying suspensions of porous-glass powders of various dispersities to special grids carrying collodion films. They were washed with water in test tubes by decantation.

The electron micrograph in Fig. 7 shows particles of the porous glass $[\mathrm{Na}\ 70-23]_{530}$; the original glass was clear. On the photograph the particles of porous glass appear to be nonporous, in spite of the fact that adsorption data indicate that more than 20% of the volume of a particle consists of pores. The explanation is that the pores are too small to be resolved by the electron microscope.

It follows from the adsorption measurements that the predominating pore radius is about 14 A and that there are no pores of radius greater than 20 A in this porous glass [7].

The electron micrograph in Fig. 8 is of the product obtained by treating the same porous glass with 0.5 N KOH for two hours. Numerous pores, fairly constant in size, are clearly visible on the photograph; they form a thin-walled honeycomb-like structure. From the micrograph in Fig. 8 the pore radius characteristic of the honeycomb structure can be estimated approximately at the value of 150 A*. According to the adsorption results the most probable value of the radius is 65 A, and according to the X-ray results 46 A.

Quite a different picture is given of alkali-treated porous glasses prepared from an opalescent glass. The electron micrograph in Fig. 9 (see plate, p. 184) is of the porous glass $[\mathrm{Na}\ 70-23]_{650}$ after treatment in 0.5 N KOH for two hours. This photograph differs from the preceding ones in that it is impossible to detect the presence of a thin-walled honeycomb structure formed from comparatively fine pores. Instead, it can be seen that many of the large particles contain pores and cavities of considerable size and irregular form separated by thick walls. It is a characteristic feature that in this case the smaller particles have no visible pores, but, as judged by their outlines, appear to be pieces that have broken away from the walls of the coarsely porous structure during the comminution of the grains of porous glass which occurred when it was gound in the preparation of the specimen. From the photograph (Fig. 9), the radii of the pores may be estimated at 300-500 A. These values are in good agreement with the results of adsorption and X-ray measurements.

The micrograph in Fig. 10 is of particles of porous glass prepared from strongly opalescent glass Na 70 − 23 (heated-treated at 700°) by the usual treatment with 3 N HCl. This sample was not treated with alkali. Adsorption measurements indicated that this porous glass has a uniform finely porous structure having pores of radius 8 A approximately. For this glass, as for those already considered, the adsorption method measures the radius of the pores in the secondary fine structure formed within the coarser structure of the silica skeleton, which can be determined by the adsorption method only after the glass has been treated with alkali. When, however, this sample was investigated by the low-angle X-ray scattering method, very large channels separated by thick walls were detected. On the electron micrograph also, pores of radius greater than 500 A are visible on some of the particles. The photograph as a whole is characterized by a fairly continuous background, which probably arises from very finely dispersed SiO_2 particles forming a thin layer on the collodion film. We are inclined to the view that this finely dispersed SiO_2 is formed by the breakdown of the secondary fine structure in some of the cells of the silica skeleton during grinding of the glass powder in a water medium in an agate mortar and during the sedimentation of the suspension. The large pores seen on the photograph are probably cells of the silica skeleton, which have been revealed here even before the glass has been treated with alkali. Hence, the electron-microscope investigations also show that there is a difference in the structure of porous glass prepared from opalescent and nonopalescent sodium borosilicate glasses.

SUMMARY

1. An investigation of porous glasses by three independent methods (by adsorption measurements, by the low-angle scattering of X-rays, and by the electron microscope) has revealed that they contain two structures: the coarser structure of the basic (silica) skeleton, and the finely porous structure formed of highly dispersed silicic acid within the channels of the skeleton.

2. The basic skeleton of porous glasses prepared from original glasses that are opalescent always contains channels, the dimensions of which are about ten times as great as those of the channels in porous glasses prepared from clear glasses.

3. When the original glasses are opalescent, the channels may be more than 1000 A in diameter, whereas

---

*This value must be regarded as somewhat high as a result of difficulties in measuring the diameters of the pores, which, in the case of fine particles, have diffuse outlines on the photograph.

when the original glasses are clear the channels are 80-160 A in diameter. The pores of the highly dispersed silicic acid are not more than 20-40 A in diameter.

Received April 2, 1954

Institute of Silicate Chemistry of the USSR
Academy of Sciences

LITERATURE CITED

[1] D. I. Levin, S. P. Zhdanov, and E. A. Porai-Koshits, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, No. 1, 31.*

[2] I. V. Grebenshchikov and O. S. Molchanova, J. Gen. Chem., 12, 588 (1942).

[3] S. P. Zhdanov, Thesis, Leningrad, 1950.

[4] A. V. Kiselev, Bull. Moscow State Univ., 11, 111 (1949).

[5] M. M. Dubinin, Physicochemical Principles of Sorption Technology, 1935.

[6] A. V. Kiselev, Prog. Chem. 14, 367 (1945).

[7] S. P. Zhdanov, Proc. Acad. Sci. USSR, 82, 281 (1952).

[8] E. A. Porai-Koshits, Prog. Phys. Sci., 39, 573 (1949).

[9] E. A. Porai-Koshits and Yu. G. Sokolov, Proc. Acad. Sci., USSR, 72, 477 (1950).

[10] E. A. Porai-Koshits, Bull. Acad. Sci. USSR, Physical Series, 15, 195 (1951).

[11] E. A. Porai-Koshits and V. N. Filipovich, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, No. 1 **

[12] E. A. Porai-Koshits, Doctorate Thesis, Leningrad, 1953.

---

* See Consultants Bureau Translation, p. 27.

** " " " " p. 19.

SYSTEMS CONTAINING HYDROGEN PEROXIDE AT HIGH CONCENTRATION.

COMMUNICATION 8. THERMAL CHARACTERISTICS AND STABILITIES OF SOLID PHASES OF THE SYSTEM $NaOH - H_2O_2 - H_2O$

S. Z. Makarov and N. K. Grigoryeva

In a study of the 0° isotherm of the system $NaOH - H_2O_2 - H_2O$ [1] we have shown that solid phases of the peroxide type, $Na_2O_2 \cdot 8H_2O$ and $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$ are present. In the literature [2] the second of these compounds $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$ is sometimes regarded as a hydroperoxide derivative $NaOOH \cdot 0.5H_2O_2 \cdot 2H_2O$, since $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O = 2[NaOOH \cdot 0.5H_2O_2 \cdot 2H_2O]$. This compound was prepared by vacuum evaporation of a solution containing 3.5-4.0 equivalents of H_2O_2 per equivalent of NaOH. The precipitated crystals were fine and clear, but gradually became opalescent. They effloresced over H_2SO_4, losing their water of crystallization and being converted into the compound $Na_2O_2 \cdot 2H_2O$, which may be treated as $2(NaOOH \cdot 0.5H_2O_2)$ or $Na_2H_4O_6$. The question arose of the synthesis of the "parent" substance, the so-called sodium hydroperoxide NaOOH.

As is well known, sodium hydroperoxide was first prepared by Tafel in 1894 [3] by the action of absolute alcohol on solid sodium peroxide:

$$Na_2O_2 + C_2H_5OH \rightarrow C_2H_5ONa + NaOOH$$

and by mixing Na_2O_2 powder with an ice-cooled mixture of C_2H_5OH and HCl:

$$Na_2O_2 + HCl + C_2H_5OH \rightarrow NaOOH + NaCl + C_2H_5OH.$$

It was noted that when warmed even very slightly the compound decomposed with evolution of oxygen: $2NaOOH \rightarrow 2NaOH + O_2$; and when it was dissolved in water: $NaOOH + H_2O \rightarrow NaOH + H_2O_2$.

Tafel called the compound NaOOH "natryl hydrate". Wolffenstein and Peltner [4] called it "trioxide hydrate" and prepared it by the action of a concentrated alcoholic solution of hydrogen peroxide on sodium ethoxide:

$$NaOC_2H_5 + H_2O_2 \rightarrow NaOOH + C_2H_5OH.$$

It should be noted, however, that although the NaOOH compounds obtained by Tafel and by Wolffenstein and Peltner were identical in composition, they behaved differently towards carbon dioxide.

Tafel's NaOOH was the more stable. D'Ans and Friederich [5] prepared NaOOH by the same method, using 98% H_2O_2. Their product always contained an excess of H_2O_2 and a little H_2O. For the purpose of comparison with the solid phases that we have found for the 0° isotherm of the system $NaOH - H_2O_2 - H_2O$, we have synthesized two samples of sodium "hydroperoxide" by Tafel's method.

EXPERIMENTAL

Heating Curves

a) Sodium Peroxide Octahydrate $Na_2O_2 \cdot 8H_2O$ (Fig. 1). Composition: active oxygen 6.70%, Na_2O 27.30%, H_2O 66.0%. When the $Na_2O_2 \cdot 8H_2O$ was heated to 60-65°, a small endothermic effect was observed. This was not associated with melting or change in composition, but corresponded to the removal of alcohol and ether. At 110-115° a large endothermic effect was observed. At this temperature the substance liquefied, being decomposed with complete loss of active oxygen and undergoing dissolution in the water of crystallization, forming the dihydrate of sodium hydroxide $NaOH \cdot 2H_2O$ of composition Na_2O 37.27% and H_2O 62.73%. When heating was continued until the temperature attained 520°, anhydrous sodium hydroxide of composition Na_2O 74.83% and H_2O 25.17% was obtained.

b) "Sodium Hydroperoxide" $2NaOOH = Na_2O_2 \cdot H_2O_2$ (Fig. 2) had the following composition (%):

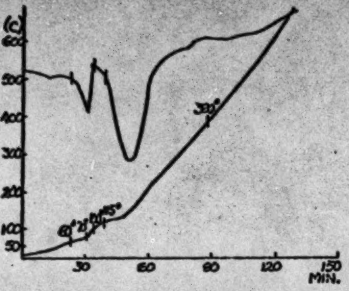


Fig. 1.

First sample:

active oxygen	23.73	NaOOH	82.28
Na_2O	55.44	NaOH	11.14
H_2O	20.83	H_2O	6.58

Second sample:

active oxygen	23.9	NaOOH	83.8
Na_2O	59.83	NaOH	15.7
H_2O	16.27	H_2O	0.5

On the heating curves two thermal effects were detected by the differential method: the first, at 55-65°, was exothermic and was associated with the evolution of active oxygen — not the whole of it, but only the part corresponding to the hydrogen peroxide, if we take the formula to be $Na_2O_2 \cdot H_2O_2$. At this temperature the substance began to cake together and it became close in composition to sodium peroxide monohydrate $Na_2O_2 \cdot H_2O$ (active oxygen 14.29%, Na_2O 63.41%, and H_2O 22.3%). The second seffect — an endothermic one, occurred at about 300° and corresponded to liquefaction. The form of the heating curve would lead us to suppose that the most probable formula for the compound is $Na_2O_2 \cdot H_2O_2$, and not NaOOH.

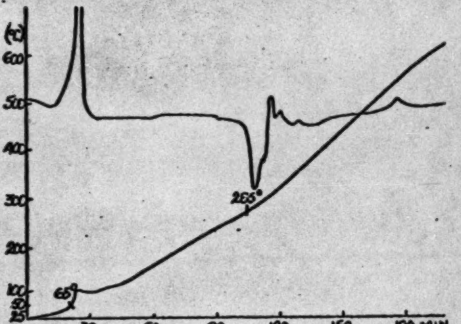


Fig. 2.

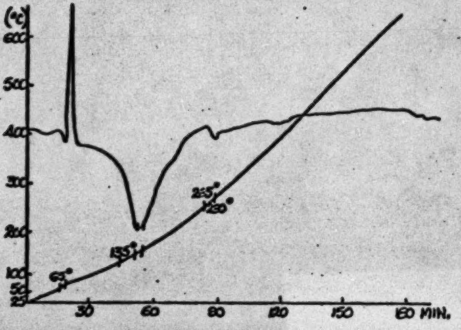


Fig. 3.

c) Sodium Peroxide Perhydrate

$NaOOH \cdot 0.5H_2O_2 = Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$ (Fig. 3). Composition: active oxygen 21%, Na_2O 23.54%, and H_2O 55.46%. The heating curve showed two effects. The first was endothermic and occurred at 60-65°. The substance then lost the whole of its active oxygen, both that of the hydrogen peroxide and that of the sodium peroxide, which dissolved with decomposition in the water of crystallization. The substance took up the following composition: no active oxygen, Na_2O 34.91%, H_2O 65%. This corresponds approximately to a hydroxide hydrate of the formula $NaOH \cdot 3.5H_2O$, which has the composition Na_2O 30.10%, H_2O 69.90%. At 135° there was an endothermic effect, after which the substance took up the composition corresponding to $NaOH \cdot H_2O$.

Thermal Stabilities of the Compounds

a) Sodium Peroxide Octahydrate

$Na_2O_2 \cdot 8H_2O$. The thermal stability of $Na_2O_2 \cdot 8\ H_2O$ was investigated at 42° and 62°. For this purpose a weighed amount of it was placed in a test tube having a side tube. The test tube was closed with a stopper carrying a thermometer, and it was then placed in a bath of a substance having a boiling point equal to the desired experimental temperature. The side tube was connected, through a U-tube containing successive columns of soda lime and calcium chloride, to a buret filled with water. The rate at which the substance decomposed was extimated by observations on the volume of water displaced by oxygen per unit time.

Temperature 42°

The original substance, sodium peroxide octahydrate, contained 6.18% of active oxygen and 25.3% of Na_2O; the amount taken was 6.8546 g. The test for thermal stability was carried out at 42° for 1 hour 30 minutes at 767 mm, the room temperature being 15°.

During the first ten minutes the evolution of oxygen was insignificant (1.4 ml), and it then stopped altogether (Table 1). After the experiment the substance contained 5.57% of active oxygen and 24.58% Na_2O, and the loss in weight was 0.0244 g. It may be considered that $Na_2O_2 \cdot 8H_2O$ is stable at 42°.

Temperature 62°

The original substance contained 6.18% of active oxygen and 25.3% of Na_2O; the amount taken was 6.0386 g; room conditions were 763 mm and 15°. The experiment was continued for three hours at 62°. After the experiment the substance contained 26.55% of Na_2O, and active oxygen was completely absent. The loss in weight was 0.3750 g and the amount of water that separated was 0.0018 g. The final product was a clear solution.

TABLE 1

Time (minutes)	Temperature (°C)	Actual amount of oxygen (ml)	Amount of oxygen at NTP (ml/g)
5	28	1.0	0.13
10	38	1.4	0.19
20	40	1.4	0.19
30	41	1.4	0.19
90	41	1.4	0.19

TABLE 2

Time (minutes)	Temperature (°C)	Amount of oxygen		
		actual (ml)	at NTP (ml/g)	Percentage of original oxygen
10	40	2.0	0.31	0.71
20	55	9.0	1.42	3.26
30	62	29.2	4.66	10.26
40	63	59.2	9.33	21.5
50	63	86.0	13.56	31.3
60	62	112.4	17.7	41.0
70	61	140.0	22.0	51.0
80	59	162.0	25.5	59.1
90	59	185.0	29.1	67.5
100	59	222.0	35.0	81.0
110	61	250.0	39.4	91.2
120	62	267.0	42.1	97.4
130	62	270.6	42.7	98.8
150	61	271.2	42.8	99.0
180	61	271.2	42.8	99.0

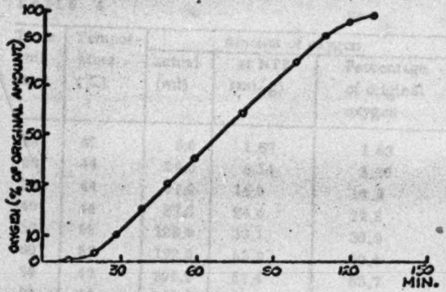


Fig. 4.

Table 2 gives the results of this experiment, and Fig. 4 shows the decomposition curve. At 62°, therefore, $Na_2O_2 \cdot 8H_2O$ is completely decomposed. According to the published results of Jaubert [6], at 30° $Na_2O_2 \cdot 8H_2O$ melts in its water of crystallization, it begins to decompose with evolution of oxygen at 30-40°, and it decomposes completely at 80-100°. Our experiments present a different picture. At 42° sodium peroxide octahydrate did not liquefy and only a very small amount of oxygen was evolved in the first few minutes. It was very stable in spite of the fact that its oxygen and Na_2O contents did not have quite the theoretical values. At 62°, complete liquefaction and decomposition of the octahydrate occurred in 90 minutes.

b) "Sodium Hydroperoxide" $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$

Temperature 30°

The original substance contained 15.3% of active oxygen and 21.94% of Na_2O; the amount taken was 6.831 g. The room conditions were 743 mm and 16°. A preliminary experiment was carried out for three days, the temperature being 30° for periods at the beginning and end of this time, and at 13-15° for the intervening 2.5 days.

After the experiment the substance contained 12.47% of active oxygen and 22.10% Na_2O. The loss in weight was 0.2892 g, and the amount of moisture that separated was 0.0112 g. The decomposition results are given in Table 3, from which it will be seen that the compound is still fairly stable at 30°. It gives up only 18.5% of its original active oxygen. and is converted at 30° into a stable compound containing 12.47% of active ogygen.

TABLE 3

Time (minutes)	Temperature (°C)	Amount of oxygen		Time (minutes)	Temperature (°C)	Amount of oxygen	
		actual (ml)	at NTP (ml/g)			actual (ml)	at NTP (ml/g)
10	30	2.2	0.29	150	35	48.7	6.5
20	31	3.8	0.50	180	33	60.5	8.17
30	31	5.3	0.71	210	32	70.0	9.40
40	31	7.1	0.96	240	31	77.0	10.40
50	31	9.9	1.30	270	31	90.3	12.1
60	31	12.9	1.75	300	31	103.5	13.9
70	31	15.3	2.06	330	31	109.0	14.6
80	31	18.1	2.44	2.5 days	13-15	129.0	17.4
100	31	24.5	3.30	+120	31	132	17.8
130	31	33.3	4.4	+240	31	132	17.8

Temperature 42°

Two experiments were carried out at this temperature. In the first a substance containing 15.30% of active oxygen and 21.94% Na_2O was used, and in the second the substance used contained 9.84% of active oxygen and 26.23% of Na_2O (the second substance had partially decomposed). The results of the first experiment are given in Table 4, and the results of the second are given in Table 5. Fig. 5 gives the decomposition curves for the two substances. In the first experiment the product finally contained 7.08% of active oxygen and 26.20% of Na_2O. In both experiments self-heating occurred with rise in temperature to 57°.

TABLE 4

Time (minutes)	Temperature (°C)	Amount of oxygen		
		actual (ml)	at NTP (ml/g)	Percentage of original oxygen
10	42	6.0	1.67	1.63
20	44	29.0	8.14	8.00
30	44	57.0	16.0	14.9
40	44	87.0	24.4	22.8
50	52	128.0	33.1	30.9
60	57	192.0	53.9	50.4
70	47	205.0	57.4	53.7
90	43	207.6	58.3	54.4
120	43	207.6	58.3	54.4

TABLE 5

Time (minutes)	Temperature (°C)	Amount of oxygen		
		actual (ml)	at NTP (ml/g)	Percentage of original oxygen
5	37.5	7.5	1.6	2.3
10	41.0	20.0	2.9	4.2
15	42.5	37.0	5.4	7.8
20	43.5	57.0	8.7	12.6
25	45.0	85.0	12.4	16.0
30	57.0	153.0	22.5	32.7
35	55.0	178.0	26.1	37.9
40	49.0	183.0	26.9	39.1
45	44.0	185.0	27.1	39.3
50	42.0	185.0	27.1	39.3
60	42.0	185.0	27.1	39.3
90	37.0	185.0	27.1	39.3

Temperature 57°

At 57° intense self-heating occurred, and threre was rapid liquefaction with much frothing. It was difficult to follow the progressive decompostion of the substance. Table 6 gives the results of this experiment. It will be seen, therefore, that at 30° $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$ decomposes partially with evolution of a part of its active oxygen; at 42° it decomposes with formation of sodium peroxide octahydrate, which is still fairly stable under these conditions; and at 57° it decomposes vigorously with rapid evolution of oxygen.

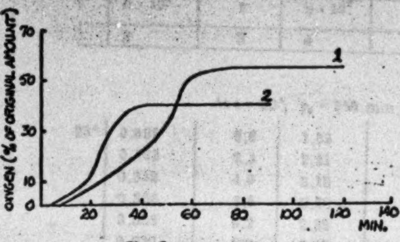


Fig. 5

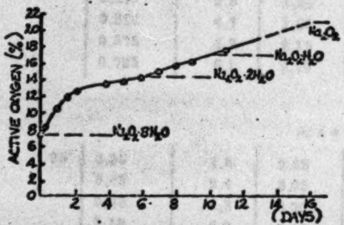


Fig. 6

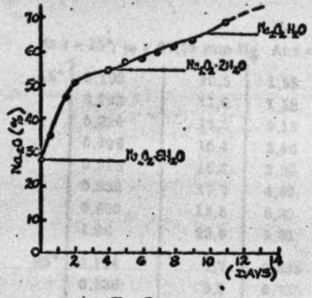


Fig. 7

TABLE 6

Time (minutes)	Temperature (°C)	Amount of oxygen	
		actual (ml)	in ml/g
5	39	5	0.84
10	47	35	5.94
15	70	175	29.5
17	63	250	42.1
18	61	270	45.5
19	60	290	48.9
20	58	The substance liquefied and frothed up	

Dehydration of $Na_2O_2 \cdot 8H_2O$*

The experiments on the dehydration of $Na_2O_2 \cdot 8H_2O$ were carried out on crystals (large plates reminiscent of mica) prepared from $NaOH \cdot H_2O$ and H_2O_2. The crystals of $Na_2O_2 \cdot 8H_2O$ were carefully pressed off on the filter and then placed in a thin layer in a Petri dish, which was placed over sulfuric acid in a vacuum desiccator. At intervals of 0.5-1 day samples were taken for analysis for the active oxygen, Na_2O, and H_2O contents, the desiccator being evacuated after removal of the sample. As the dehydration process proceeded, the large clear crystals of $Na_2O_2 \cdot 8H_2O$ were converted into small pale-yellow opaque crystals, and the yellowish color characteristic of anhydrous sodium peroxide gradually became more intense. The final product was found by analysis to have a composition close to $Na_2O_2 \cdot H_2O$. The analytic results for this experiment, which lasted for eleven days, are given in Table 7.

The variation of the content of active oxygen with time is shown in Fig. 6, and the variation in the Na_2O content in Fig. 7. Both diagrams show clearly that the dehydration of $Na_2O_2 \cdot 8H_2O$ goes as far as $Na_2O_2 \cdot 2H_2O$ in the course of 4-5 days, and as far as $Na_2O_2 \cdot H_2O$ in ten days.

SUMMARY

1. An investigation has been made, with the aid of heating curves, of the thermal stabilities and dehydration behavior of the solid phases found in the ternary system $NaOH - H_2O_2 - H_2O$ at 0°, namely $Na_2O_2 \cdot 8H_2O$ and $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$, and also of the so-called "sodium hydroperoxide" NaOOH or $Na_2O_2 \cdot H_2O_2$, which was synthesized by Tafel's method.

2. The compound $Na_2O_2 \cdot 8H_2O$ is undoubtedly a hydrated form of sodium peroxide. This view is confirmed by the occurrence of endothermic dehydration effects, and by the curves for the dehydration of $Na_2O_2 \cdot 8H_2O$, which pass through the stages $Na_2O_2 \cdot 8H_2O$, $Na_2O_2 \cdot 2H_2O$, and $Na_2O_2 \cdot H_2O$.

3. The compound $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$ is of lower stability. Its heating curve has a very marked exothermic maximum at 60-65° characteristic of perhydrate compounds. The temperature at which complete decomposition occurs is the same as the decomposition temperature of $Na_2O_2 \cdot 8H_2O$.

4. The existing data on the properties of the so-called "sodium hydroperoxide" NaOOH support the view that this compound should be regarded as $Na_2O_2 \cdot H_2O_2$.

---

* The experimental work was carried out by I. F. Bulycheva.

BLANK
PAGE

BLANK
PAGE

TABLE 1

t°	$h \cdot 10^2$	π	$h \cdot 10^2$	π	$h \cdot 10^2$	π	$h \cdot 10^2$	π	$h \cdot 10^2$	π
1	2	3	4	5	6	7	8	9	10	11
Diethyl ether At t = 25°, p_0 = 550 mm Hg; At t = 40°, p_0 = 955 mm Hg										
25°	0.085	0.6	1.32	10.8	4.16	21.5	20.0	37.4	42.7	47.7
	0.182	2.3	2.21	13.9	4.67	21.6	20.8	38.0	48.0	51.3
	0.352	4.0	2.18	14.2	6.60	24.5	24.0	39.6	51.5	51.3
	0.368	3.8	2.63	16.0	7.25	25.6	30.2	42.8	57.0	52.8
	0.638	6.2	2.82	16.5	8.67	27.3	30.9	42.9		
	0.930	8.2	3.40	18.3	9.55	28.7	36.3	44.8		
	1.23	10.3	3.80	19.4	15.5	33.5	41.0	47.1		
40°	0.0014	0.1	0.793	5.7	2.70	15.3	6.32	23.3	22.9	37.8
	0.191	2.5	1.26	9.7	3.17	17.5	6.45	23.6	25.1	39.2
	0.526	4.7	1.95	12.7	3.32	17.8	6.45	24.1	26.4	40.4
	0.575	4.7	2.19	12.5	4.03	18.9	11.5	30.0	29.5	41.6
	0.725	6.1	2.19	19.9	5.00	20.9	17.4	33.6		
Acetone At t = 25°, p_0 = 255 mm Hg										
25°	0.36	1.5	2.28	10.0	6.62	18.1	22.3	32.3	51.2	51.2
	0.48	2.4	3.05	10.6	7.05	17.4	28.9	37.2	53.5	51.7
	0.76	4.3	3.20	12.3	8.39	19.1	33.2	40.6	60.0	55.9
	1.13	5.2	3.47	11.8	9.33	20.7	35.6	42.1	66.2	59.5
	1.16	5.7	4.38	13.5	11.0	21.9	41.8	45.5	73.4	61.4
	1.35	6.9	5.27	15.6	13.9	25.0	45.5	49.2	79.9	65.2
	2.22	7.9	5.70	16.2	17.4	28.5	50.3	51.4	100.0	75.2
Heptane At t = 15°, p_0 = 27.55 mm Hg At t = 25°, p_0 = 47.65 mm Hg, At t = 40°, p_0 = 92.05 mm Hg										
15°	0.192	10.5	1.58	26.1	6.68	40.7	26.9	54.4	71.3	66.9
	0.203	11.0	1.58	28.7	7.65	40.9	31.3	56.5	79.5	67.9
	0.224	11.5	2.18	29.8	9.32	42.7	34.2	57.6	95.5	71.6
	0.406	15.4	3.46	33.7	13.5	47.9	37.6	59.4	100.0	72.8
	0.515	16.6	3.96	33.9	14.1	47.9	41.0	60.1		
	0.632	17.7	4.82	37.5	17.7	49.4	49.7	61.8		
	0.660	18.5	5.30	38.8	20.4	55.1	60.5	64.9		
	1.26	23.9	5.80	39.9	23.2	53.2	65.4	65.9		
25°	0.124	7.7	0.635	17.2	4.65	35.0	13.5	45.3	40.0	56.7
	0.136	8.5	0.735	17.7	5.82	36.0	14.8	45.4	46.0	57.9
	0.195	10.4	0.872	20.4	6.50	37.3	18.0	47.1	57.4	60.0
	0.196	10.3	1.01	21.4	8.55	40.0	19.8	47.6	60.7	61.3
	0.236	10.8	1.66	25.1	8.97	39.2	21.5	49.0	73.0	63.4
	0.258	12.2	2.00	27.7	9.40	39.7	23.6	50.4	93.6	68.6
	0.318	13.3	2.94	31.3	10.2	42.7	28.4	52.8	96.0	69.5
	0.477	16.0	3.40	32.2	12.3	45.2	30.0	53.1	98.0	71.0
40°	0.108	6.0	2.64	26.2	6.12	33.1	11.6	38.6	21.4	43.7
	0.195	7.8	3.06	28.0	6.40	33.7	12.5	39.0	27.4	47.2
	0.326	9.9	3.94	30.5	7.00	34.5	13.5	39.5	32.6	49.1
	0.445	12.0	4.05	29.4	7.69	35.2	15.0	40.5	35.6	50.6
	0.640	14.1	5.15	32.2	8.05	35.8	15.7	41.0		
	1.14	18.0	5.32	32.2	8.82	36.4	17.2	41.9		
	1.86	23.2	5.58	32.3	11.6	37.9	19.8	43.5		

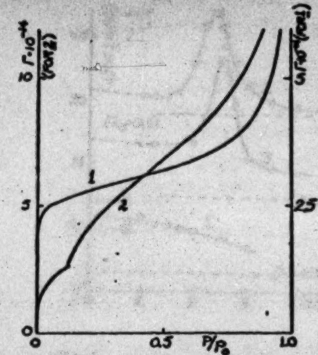


Fig. 1.

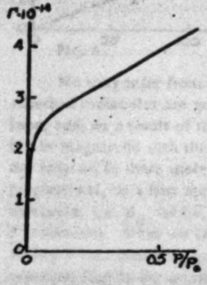


Fig. 2.

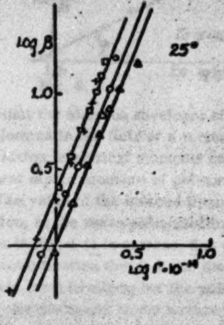


Fig. 3.

(μ_e is the effective dipole moment of a molecule oriented normally to the adsorbent surface). Equation 3 leads to the following equation for the adsorption isotherm:

$$\ln \frac{\Gamma}{p} = \ln H - \frac{7.5}{kT}\ \mu_e^2 \Gamma^{3/2}, \tag{4}$$

(H is the integration constant). The equation for the surface-pressure isotherm corresponding to Equation 3 cannot be obtained analytically in an explicit form.

When an examination is made of adsorption at energetically homogeneous surfaces, it can be shown [7] that the sign of the slope of the adsorption isotherm in its initial part is determined by the sign of the forces of interaction between the adsorbed molecules; repulsive forces should give convex isotherms, and attractive forces should give concave isotherms. The convex isotherms of the substances now under consideration indicate a predominance of repulsive forces in the surface layer, so that for these substances it is logical to use the very simple scheme of dipole interaction described by Equation 3.

For the purpose of the quantitative verification of the applicability of Equation 3, it may be presented in the following form:

$$\log \beta = \log(\pi - kT\Gamma) = \log 4.5\,\mu_e^2 + \frac{5}{2}\ \log\ \Gamma, \tag{5}$$

(β is the departure of the actual isotherm of state from the ideal isotherm, which would be given by an ideal two-dimensional gas). If we transform the values of π and Γ into the coordinates log β and log Γ, then if Equation 3 is obeyed we must obtain a straight line of slope 5/2, and the intercept on the axis of ordinates will enable the value of μ_e to be determined.

Fig. 3 shows the results of this construction for heptane (□), diethyl ether (O), and acetone (Δ), calculated from our data, and for toluene (+), calculated from Kemball's data, the straight lines being drawn at the theoretical slope of 5/2. As will be seen from Fig. 3, Equation 3 is closely obeyed in the monomolecular region by these substances. At higher values of Γ the curves depart from straight lines owing to increase in the effectiveness of attractive forces and to transition to polymolecular adsorption.

For these substances, therefore, Equations 1 and 3 are obeyed simultaneously. It is easy to see that this fact follows from the forms of the two equations. Thus, if Equation 1 is presented in the form:

$$\pi = kT\Gamma + kT\Omega \frac{\Gamma^2}{1-\Omega\Gamma}\ . \tag{6}$$

it becomes evident that it must approximate closely to Equation 3. Hence, whenever Equation 1 is obeyed, Equation 3 also must be obeyed. From the intersects on the axis of ordinates (Fig. 3), the effective dipole moments were calculated. The resulting values of μ_e are given in Table 2 together with the permanent dipole moments μ and the values of the mean polarizabilities of the molecules, $\overline{b} = {}^1/_3\,(b_1 + b_2 + b_3)$, b_1, b_2, b_3 are the principal axes of the polarization ellipsoid.

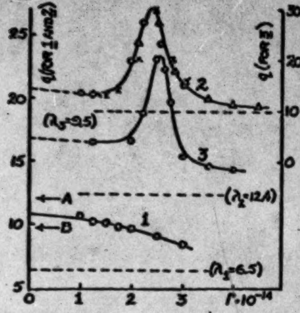


Fig. 5.

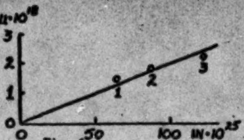


Fig. 4.

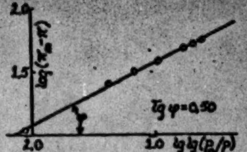


Fig. 6.

We may infer from Table 2 that the electron envelopes of the adsorbed molecules are greatly deformed in the field at a mercury surface, and, as a result of the polarization, electrical moments comparable in magnitude with the permanent dipole moments of polar molecules are induced in these molecules. The value of the induced moment is proportional, to a first approximation, to the mean polarizability of the molecule, i.e. $\mu_e \approx C\bar{b}$, as shown in Fig. 4 (1 is acetone, 2 is ether, and 3 is toluene). When we take into consideration that it is not the polarizability $\bar{b}$ that should be used in these considerations, but the polarizability corresponding to the orientation of the molecules in the surface layer, and that the value of μ_e is determined by this method with low accuracy, the approximate proportionality between μ_e and $\bar{b}$ must be regarded as a weighty argument in favor of the concepts that we have discussed. In this connection we may note that Mignolet [8] has recently shown that surface potentials of +0.16–0.27 V occur when CH_4, C_2H_2, C_2H_4, and C_2H_6 are adsorbed at a mercury surface, and he concluded that the molecules of these substances are strongly polarized in the field of the mercury surface.

The low value of μ_e for acetone is noteworthy, for it is considerably less than the permanent dipole moment μ = 2.73 D. This fact probably indicates that the acetone molecule, when adsorbed, makes contact with the mercury surface with three C atoms and an O atom, so that the permanent moment, which is localized in the CO group, is oriented parallel to the mercury surface.

With a view to a further verification of Equation 3 and of the proposed model of a nonlocalized adsorption layer, we have calculated the curves showing the dependence of the differential heats of adsorption on the coverage of the surface for the case of diethyl ether. For this purpose we applied the Clausius-Clapeyron equation to the 15° and 25° isotherms. The results of these calculations are shown by the circles on Curve 1 in Fig. 5

TABLE 2

Substance	μ_e (Debye units)	μ (Debye units)	$\bar{b} \cdot 10^{25}$ CGS units
Toluene	2.2	0.4	123
Heptane	2.2	0.0	–
Diethyl ether	1.8	1.14	88
Acetone	1.5	2.73	64

If we assumed that to a first approximation the value of μ_e is independent of temperature, then finding $(d \ln p/dT)_\Gamma$, from Equation 4 and substituting this derivative in the Clausius-Clapeyron equation, we obtain the following equation from the dependence of the differential heat of adsorption q on Γ:

$$q = \left(\frac{d \ln H}{dT}\right)_\Gamma - 7.5\,\mu_e^2 N \Gamma^{3/2} = q_0 - 7.5\,\mu_e^2 N \Gamma^{3/2}, \quad (7)$$

(N is Avogadro's number).

For the given case, Equation 7 enables us to determine the variation of q with the coverage of the surface from a single adsorption isotherm. Curve 1 in Fig. 5 was constructed with the aid of Equation 7. The values of $q_0 - q$ calculated by Equation 7 were represented as a function of Γ, and the resulting curve was displaced in a direction parallel to the axis of ordinates until it coincided with the points indicated by the circles. Simultaneously, the values of Γ were expressed in the ordinates log (Γ/p) and $\Gamma^{3/2}$ for 15° and 25°, and from the linear graphs obtained (corresponding to Equation 4) the intercepts H_1 and H_2 on the axis of ordinates were determined. From these intercepts the value of $q_0 \approx \Delta \ln H/\Delta T$ was found. This calculation of q_0 cannot be particularly accurate owing to the closeness of H_1 and H_2 in value. The arrows A and B in Fig. 5 indicate the limits of possible error in the determination of q_0. Hence, the curve q = q(Γ) in Fig. 5 confirms the validity of Equation 3 and of the assumption of the substantial independence of μ_e on temperature.

The values of q were calculated also for heptane. Results of the calculation from the Clausius-Clapeyron equation are indicated by circles (calculated from the 15° and 40° isotherms) and triangles (15° and 25° isotherms) on Curve 2 in Fig. 5. For heptane the curve q = q (Γ) is characterized by a sharp maximum at a coverage θ of about 1. In order to be more certain that this maximum is not the result of errors in the calculation of Γ, we calculated q directly from two π = π(lg h) curves corresponding to different temperatures. For this purpose, we calculated the integral heats of adsorption $\underline{Q}$ from William's equation [9]

$$Q = \pi - T\left(\frac{d\pi}{dT}\right)_p \tag{8}$$

and then found the corresponding values of the differential heats $q = \frac{dQ}{d\Gamma}$ by graphical differentiation of the curve obtained, $Q = Q(\Gamma)$; these values are shown by crosses on Curve 2 in Fig. 5. Comparison of the results of the two methods of calculation leaves no doubt about the reality of this maximum. A similar maximum was obtained when q was calculated from the 25° and 50° isotherms $\pi = \pi(\log h)$ for butyl alcohol (Curve 3 in Fig. 5). It should be noted that the initial heats of adsorption of the two isomers, butyl alcohol and diethyl ether, differ by approximately 6 kcal per mole, i.e. by an amount of the same order as the difference in the latent heats λ, and also, probably, as the energy of the hydrogen bond in butyl alcohol.

In recent years there have been several papers relating to the investigation of adsorption at homogeneous surfaces, and in these maxima have been found on the $q = q(\Gamma)$ curves for a coverage of $\theta \approx 1$, and sometimes for $\theta \approx 2$. We may mention here papers by Orr [10], who appears to have been the first to observe such maxima in a study of the adsorption of argon, oxygen, and nitrogen on potassium chloride and cesium iodide, by Rhodin [11], who examined the adsorption of nitrogen at the surface of copper monocrystals, and by Beebe and Young [12], who made a calorimetric study of the adsorption of argon on Graphon, a crystalline preparation of carbon, and found maxima at $\theta = 1$ and $\theta = 2$ on the $q = q(\Gamma)$ curves. Also, in an investigation by one of the authors of this paper and Serpinsky [13], a maximum value of q was found for the adsorption of nitrogen on sodium chloride at −195°.

A consideration of these examples, together with the examples of maxima in the adsorption of heptane, butyl alcohol, and water on mercury, tends to suggest that the appearance of maxima in the region of $\theta = 1$ on $q = q(\Gamma)$ curves for adsorption at homogeneous surfaces is the rule, rather than the exception. At high degrees of coverage Van der Waals attractive forces between adsorbed molecules begin to be significant, for they become appreciable when the intermolecular distances become small, and they grow much more rapidly than the electrostatic forces of dipole repulsion.

In conclusion we will make a somewhat more detailed examination of polymolecular adsorption at a mercury surface, taking the example of methanol, for which such adsorption is particularly characteristic. For this substance, which has small polar molecules, the adsorbed film is already 8-10 layers thick when $h = 0.9$. In view of the nonapplicability of Brunauer, Emmett, and Teller's equation for polymolecular adsorption to the adsorption isotherms of the substances that we have studied, it is of interest to determine to what extent the data for methanol satisfy the equation for polymolecular adsorption derived by Frenkel [14], and independently by Halsey and Hill (see, for example, [5]), on the assumption that the potential of the interaction forces between a molecule and a plane surface falls off (as suggested by London) with distance according to an inverse cube law. This equation has the form:

$$\ln \frac{p_0}{p} = \frac{K}{\nu^3} \approx \frac{K'}{\Gamma^3} \quad . \tag{9}$$

($\underline{K}$ is a constant, and ν is the number of layers). For thick layers Γ is proportional to ν).

It is readily shown with the aid of the Gibbs adsorption equation that Equation 9 for the adsorption isotherm corresponds to the following surface-pressure isotherm:

$$\log\ (\pi_m - \pi) = \log C + \frac{2}{3} \log\left(\log \frac{p_0}{p}\right). \tag{10}$$

(C is a constant, and π_m is the value of π when $h = 1$. If Equation 9 is obeyed, then when the experimental values of π in the polymolecular region are expressed in the coordinates $\log(\pi_m - \pi)$, $\log\left(\log \frac{p_0}{p}\right)$, we should obtain a straight line of slope 2/3. Fig. 6 shows the results of the verification of Equation 10 for methanol at 25°. The experimental points fit satisfactorily to a straight line, but its slope is not 2/3, but almost exactly 1/2. It will be readily seen that if the slope is 1/2 we obtain the following equation for polymolecular adsorption instead of Equation 9:

$$\ln \frac{p_0}{p} = \frac{B}{\Gamma^2} \quad . \tag{11}$$

which differs from Harkins and Jura's equation [15] in the absence of a constant term.

Bowers [16] measured the adsorption of gases on aluminum foil at low temperatures by the gravimetric method, and found that Equation 9 was closely obeyed by nitrogen. Later, however, in a study of the adsorption of helium on aluminum foil, Bowers [17] showed that the dependence of the thickness Δ of a polymolecular film of helium on the distance $\underline{d}$ of the given point on the surface of the adsorbent from the level of the liquid helium was given by the formula:

$$\Delta = Kd^{-1/n} \qquad (12)$$

in which $\underline{n}$ was found to be 2.0 ± 0.3.

Since the relation of the relative presure over the surface of a liquid to the height $\underline{d}$ is given by the barometric formula, Equation 12 will reduce to Equation 11 when $n = 2$.

Hence the polymolecular adsorption of methanol on mercury and of helium on aluminum is described by Equation 11, and not Equation 9. On the basis of this result, however, it would be premature to speak of the nonapplicability of Equation 9 in the analysis of polymolecular adsorption at smooth surfaces. It is clear that the matter demands further study.

The authors are deeply grateful to V. V. Serpinsky, M. M. Dubinin, B. V. Ilyin, and A. I. Sarakhov for their interest in the work, their valuable advice, and their help in organizing the investigation.

SUMMARY

1. It has been shown that an equation of state derived for nonlocalized adsorption and taking into account the electrostatic repulsive forces between identically oriented dipole molecules is applicable to the adsorption of diethyl ether, acetone, heptane, and toluene on mercury. It has been shown also that when this equation is obeyed Volmer's equation must also be obeyed. The equation has been further verified by calculating the heats of adsorption of diethyl ether.

2. There is reason to suppose that, when acetone, toluene, heptane, and diethyl ether are adsorbed on mercury, dipole moments are induced in the molecules of these substances, and these moments are comparable in magnitude to the permanent moments of polar molecules.

3. There are maxima on the curves showing the dependence of the differential heat of adsorption on surface coverage for heptane, butyl alcohol, and water, and these are found at a degree of coverage of approximately unity.

4. It has been shown that in the polymolecular adsorption of methanol on mercury the equation of Frenkel, Halsey, and Hill is not obeyed and that the experimental data for this case are in close accord with the results of direct measurements of the polymolecular adsorption of helium on aluminum.

Received May 26, 1954

Institute of Physical Chemistry of the USSR
Academy of Sciences

LITERATURE CITED

[1] B. P. Bering and K. A. Ioileva, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, No. 1, 9.*
[2] B. P. Bering and K. A. Ioileva, Proc. Acad. Sci. USSR, 93, 85 (1953).
[3] C. Kemball, E. K. Rideal, Proc. Roy. Soc. 187 A, 53 (1946).
[4] C. Kemball, Proc. Roy. Soc. 187 A, 73 (1946); 190 A, 117 (1947).
[5] M. H. Polley, W. D. Schaeffers, W. R. Smith, J. Phys. Chem. 57, 469 (1953).
[6] B. P. Bering and V. V. Serpinsky, Proc. Acad. Sci. USSR, 79, 273 (1951).
[7] B. P. Bering and V. V. Serpinsky, Problems of Kinetics and Catalysis, 7, Acad. Sci. USSR Press, Moscow and Leningrad, 1949, 383.
[8] J. C. P. Mignolet, J. Chem. Phys. 21, 1298 (1953).
[9] A. M. Williams, Proc. Roy. Soc. (Edinburgh) 38, 23 (1918).
[10] W. J. C. Orr, Trans. Faraday Soc. 35, 1247 (1939); Proc. Roy. Soc. 173 A, 349 (1939).
[11] T. N. Rhodin, J. Am. Chem. Soc. 72, 5102 (1950); 73, 3143 (1951).
[12] R. A. Beebe, D. M. Young, J. Phys. Chem. 58, 93 (1954).
[13] B. P. Bering and V. V. Serpinsky, Proc. Acad. Sci. USSR, 94, 497 (1954).
[14] Ya. I. Frenkel, Kinetic Theory of Liquids, Acad. Sci. USSR Press, Moscow and Leningrad, 1945.
[15] W. D. Harkins, C. Jura, J. Chem. Phys. 12, 112 (1944).
[16] R. Bowers, Phil. Mag. 44, 467 (1953).
[17] R. Bowers, Phys. Rev. 91, 1016 (1953).

---

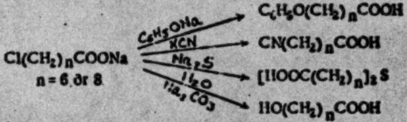
* See Consultants Bureau Translation, p. 7.

ω-CHLORO CARBOXYLIC ACIDS, AND SOME OF THEIR REACTIONS

A. N. Nesmeyanov and L. I. Zakharkin

Whereas the higher ω-bromo carboxylic acids $Br(CH_2)_nCOOH$ have received fairly detailed investigation and are widely applied in various syntheses, the corresponding ω-chloro carboxylic acids have received comparatively little study, probably because it is considered that the chlorine atom in these compounds is of low reactivity, and also because of the difficulty of preparing them. Recently, however, a convenient method has been found for the synthesis of some of the ω-chloro carboxylic acids. It consists in the hydrolysis of α,α,α,ω-tetrachloroalkanes $Cl(CH_2CH_2)_nCCl_3$ with concentrated sulfuric acid. These chloro compounds are prepared by the reaction of ethylene with carbon tetrachloride under pressure [1, 2], and they give acids having odd numbers of carbon atoms. By this method 5-chlorovaleric, 7-chloroheptanoic, and 9-chlorononanoic acids have been prepared from 1,1,1,5-tetrachloropentane, 1,1,1,7-tetrachloroheptane, and 1,1,1,9-tetrachlorononane respectively [1, 3]. In the present investigation we have isolated the succeeding tetrachloroalkanes from the products of the reaction of ethylene with carbon tetrachlorides, and by hydrolysis of these we have prepared 11-chloroundecanoic, 13-chlorotridecanoic, and 15-chloropentadecanoic acids. We have investigated some of the reactions of these ω-chloro carboxylic acids, and have shown that they can be used successfully instead of the corresponding bromo acids. When the ethyl esters of 5-chlorovaleric and 7-chloroheptanoic acids were treated with sodium alkoxide, the corresponding alkoxy esters were obtained. The reaction of the same ethyl esters with sodiomalonic ester in presence of sodium iodide gave high yields of the triethyl esters of 1,1,5-pentanetricarboxylic and 1,1,7-heptanetricarboxylic acids, which yielded pimelic and azelaic acids respectively when hydrolyzed with dilute hydrochloric acid.

It was found that salts of 7-chloroheptanoic and 9-chlorononanoic acids readily reacted in aqueous solution with sodium phenoxide, and with sodium cyanide; they were hydrolyzed in presence of bases into ω-hydroxy carboxylic acids. In collaboration with Petrova [4] we have shown previously that both of these chloro acids readily react with sodium sulfide in aqueous solution and yield the corresponding ω,ω'-thio dicarboxylic acids.



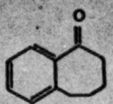
Oxidation of 7-hydroxyheptanoic acid with concentrated nitric acid gave pimelic acid in high yield. Hydrogenation of 7-cyanoheptanoic in ammoniacal solution in presence of Raney nickel yielded 8-aminooctanoic acid. When, however, salts of 5-chlorovaleric acid were treated with sodium phenoxide or sodium cyanide in aqueous solution, the corresponding derivatives were not formed, the product being δ-valerolactone (or 5-hydroxyvaleric acid), which does not react further under these conditions. On the other hand, with the sodium salt of benzenethiol 5-chlorovaleric acid gave a good yield of 5-(phenylthio)valeric acid. It was found that 5-phenoxyvaleric acid could be obtained from 5-chlorovaleric acid only via δ-valerolactone by heating the latter with anhydrous sodium phenoxide at high temperature, the reaction being analogous to the preparation of 4-phenoxybutyric acid from γ-butyrolactone [5].

7-Chloroheptanoic acid was converted into the trimethylbetaine of 7-aminoheptanoic acid, and so, by cleavage of the latter with alkali, into 6-heptenoic acid:

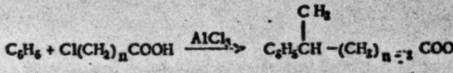
$$Cl(CH_2)_6COOH \rightarrow (CH_3)_3\overset{+}{N}(CH_2)_6COO^- \xrightarrow{NaOH} CH_2=CH-(CH_2)_4COOH + (CH_3)_3N.$$

We have studied the reaction of ω-chloro carboxylic acids with benzene in presence of aluminum chloride. It has been shown previously [6] that 4-chlorobutyric acid reacts with benzene to give 4-phenylbutyric acid. In a similar way, 5-chlorovaleric acid in presence of aluminum chloride at a molar ratio of 1:1 gave a high yield of 5-phenylvaleric acid. When the amount of aluminum chloride was increased, in addition to 5-phenylvaleric acid 1-benzosuberanone was formed:

$$C_6H_6 + Cl(CH_2)_4COOH \xrightarrow{AlCl_3} C_6H_5(CH_2)_4COOH +$$



It should be noted that the yield of 5-phenylvaleric acid obtained from 5-chlorovaleric acid was higher than that which has been obtained from δ-valerolactone [7]. Unlike the lower acids, 7-chloroheptanoic, 9-chlorononanoic, and 11-chloroundecanoic acids reacted with benzene in presence of aluminum chloride with isomerization, for the resulting "phenylheptanoic", "phenylnonanoic", and "phenylundecanoic" acids were found to be different from the known 7-phenylheptanoic acid [8], 9-phenylnonanoic acid [9], and 11-phenylundecanoic acid [10] respectively. When the "phenylnonanoic" and "phenylheptanoic" acids were oxidized in acetic acid with chromic anhydride, acetophenone was isolated*, which indicates the presence of the grouping $C_6H_5CH(CH_3)$ in the acids. The structure of the central part of the molecule has not been investigated. It is probable that for these acids reaction proceeds by the scheme:



$$C_6H_6 + Cl(CH_2)_nCOOH \xrightarrow{AlCl_3} C_6H_5CH(CH_3)-(CH_2)_{n-2}COOH,$$

(n = 6, 8 or 10).

The condensation of 5-chlorovaleryl and 7-chloroheptanoyl chlorides with benzene in presence of aluminum chloride went in the normal fashion and yielded the corresponding ω-chloroalkanophenones:

$$C_6H_6 + ClCO(CH_2)_nCl \xrightarrow{AlCl_3} C_6H_5CO(CH_2)_nCl,$$

(n = 4 or 6).

With the object of characterizing the ω-chloro carboxylic acids discussed above, some of their derivatives were prepared.

EXPERIMENTAL

For the preparation of the α,α,α,ω-tetrachloroalkanes, the reaction of ethylene with carbon tetrachloride was carried out as already described [1].

5-Chlorovaleric Acid was prepared by hydrolysis of 1,1,1,5-tetrachloropentane by the method already described [1,3]. Its amide melted at 78-79° (from benzene).

Found %: N 10.45; 10.52

$C_5H_{10}ClNO$. Calculated %: N 10.33

Its anilide melted at 108-109° (from benzene).

Found %: N 6.67; 6.59

$C_{11}H_{14}ClNO$. Calculated %: N 6.63

7-Chloroheptanoic Acid was prepared by hydrolysis of 1,1,1,7-tetrachloroheptane by the method already described [1, 3]. Its ethyl ester boiled at 122-123° (11 mm) and had n_D^{20} 1.4392; d_4^{20} 1.0110; found MR 50.10; calculated MR 50.27.

Found %: C 56.24; 56.30; H 8.95; 8.84

$C_9H_{17}ClO_2$. Calculated %: C 56.10; H 8.83

Its anilide melted at 85-86° (from benzene).

Found %: N 5.83; 5.87

$C_{13}H_{18}ClNO$. Calculated %: N 5.86

Its amide melted at 82-83° (from benzene).

Found %: N 8.46; 8.48

$C_7H_{14}ClNO$ Calculated %: N 8.57

9-Chlorononanoic Acid was prepared by hydrolysis of 1,1,1,9-tetrachlorononane by the method already described [1,3]. It melted at 29-30° (from petroleum ether). Its ethyl ester boiled at 136-137° (8 mm) and had

---

[*] Oxidation of 5-phenylvaleric acid under like conditions yields 4-benzoylbutyric acid.

n_D^{20} 1.4434; d_4^{20} 0.9854; found MR 59.37; calculated MR 59.51

Found %: C 59.72; 59.60; H 9.42; 9.52
$C_{11}H_{21}ClO_2$. Calculated %: C 59.84; H 9.58

Its acid chloride boiled at 100-101° (3 mm). Its amide melted at 76-77° (from benzene).

Found %: N 7.40; 7.58
$C_9H_{18}ClNO$. Calculated %: N 7.32

Its anilide melted at 95-96° (from methanol).

Found %: N 5.16; 5.12
$C_{15}H_{22}ClNO$. Calculated %: N 5.04

Its nitrile boiled at 105-106° (1.5 mm) and had n_D^{20} 1.4512; d_4^{20} 0.9695; found MR 48.21; calculated MR 48.44.

Found %: N 8.22; 8.16
$C_9H_{16}ClN$. Calculated %: N 8.07

11-Chloroundecanoic Acid. 1,1,1,11-Tetrachloroundecane boiled at 141-142° (3 mm) and had n_D^{20} 1.4822; d_4^{20} 1.1558; found MR 72.55; calculated MR 72.46.

Found %: C 45.06; 45.08; H 6.89; 6.77
$C_{11}H_{20}Cl_4$. Calculated %: C 44.96; H 6.80

A mixture of 77 g of the tetrachloroundecane and 250 g of concentrated sulfuric acid (92-93%) was vigorously stirred and heated in a water bath for 90 minutes. In the course of this time almost the theoretical amount of hydrogen chloride was evolved. The reaction mixture was cooled and poured onto ice, and the chloroundecanoic acid was extracted with carbon tetrachloride. The extract was washed twice with water and dried with calcium chloride. When the solvent was removed, the residue crystallized out, but vacuum distillation was found to be essential for the purification of the chloro acid. The yield of 11-chloroundecanoic acid was 41.2 g (71.5%). It boiled at 149-151° (1.5 mm) and melted at 41-42° (the literature [11] gives 39-40°).

Found %: C 59.94; 59.82; H 9.43, 9.56
$C_{11}H_{21}ClO_2$. Calculated %: C 59.86; H 9.52

Its ethyl ester boiled at 133.134° (3 mm) and had n_D^{20} 1.4469; d_4^{20} 0.9646; found MR 68.68; calculated MR 68.75

Found %: C 62.92; 62.90; H 10.05; 10.16
$C_{13}H_{25}ClO_2$. Calculated %: C 62.75; H 10.12

Its acid chloride boiled at 133-134° (4.5 mm). Its amide melted at 89-90° (from benzene).

Found %: N 6.42; 6.48
$C_{11}H_{22}ClNO$. Calculated %: N 6.37

Its anilide melted at 69-70° (from methanol).

Found %: N 4.66; 4.76
$C_{17}H_{26}ClNO$. Calculated %: N 4.89

Its nitrile boiled at 125-126° (1.5 mm) and had n_D^{20} 1.4550; d_4^{20} 0.9505; found MR 57.52; calculated MR 57.68

Found %: N 7.13; 7.06
$C_{11}H_{20}ClN$. Calculated %: N 6.96

13-Chlorotridecanoic Acid. 1,1,1,13-Tetrachlorotridecane boiled at 152-153° (1.5 mm) and had n_D^{20} 1.4842, d_4^{20} 1.1290; found MR 81.63; calculated MR 81.70

Found %: C 48.56; 48.69; H 7.28, 7.41; Cl 43.91
$C_{13}H_{24}Cl_4$. Calculated %: C 48.47; H 7.45; Cl 44.08

Hydrolysis of the tetrachlorotridecane gave 13-chlorotridecanoic acid in 42% yield. The reaction was accompanied by considerable resinification. 13-Chlorotridecanoic acid melted at 52-53° (from petroleum ether).

Found %: C 62.98; 62.96; H 10.25; 10.16

$C_{13}H_{25}ClO_2$. Calculated %: C 62.83; H 10.05

Its ethyl ester boiled at 147-149° (1.5 mm) and had n_D^{20} 1.4535; d_4^{20} 0.9604; found MR 77.92; calculated MR 77.99

Found %: C 65.18; 65.28; H 10.56; 10.42

$C_{15}H_{29}ClO_2$. Calculated %: C 65.06; H 10.55

Its acid chloride boiled at 146-147° (1.5 mm). Its anilide melted at 70-71° (from methanol).

Found %: N 4.40; 4.43

$C_{19}H_{30}ClNO$. Calculated %: N 4.32

15-Chloropentadecanoic Acid. 1,1,1,15-Tetrachloropentadecane boiled at 176-178° (1 mm) and had n_D^{20} 1.4858; d_4^{20} 1.1078; found MR 90.75; calculated MR 90.94

Found %: C 51.30; 51.26; H 7.77; 7.60

$C_{15}H_{28}Cl_4$. Calculated %: C 51.43; H 8.00

Hydrolysis of the tetrachloropentadecane gave 15-chloropentadecanoic acid in 24% yield. It melted at 62-63° (from petroleum ether).

Found %: C 65.03; 65.22; H 10.63; 10.75

$C_{15}H_{29}ClO_2$. Calculated %: C 65.13; H 10.49

Its ethyl ester boiled at 168-170° (1.5 mm) and melted at 31.5-32.5° (from petroleum ether).

Found %: C 66.83; 66.88; H 10.98; 10.82

$C_{17}H_{33}ClO_2$. Calculated %: C 66.95; H 10.90

Its acid chloride boiled at 165-166° (1.5 mm) and melted at 30-31° (from petroleum ether). Its anilide melted at 79-80° (from methanol).

Found %: N 4.08; 4.06

$C_{21}H_{34}ClNO$. Calculated %: N 3.98

Ethyl 5-Ethoxyvalerate. A mixture of 50 g of ethyl 5-chlorovalerate and sodium ethoxide (prepared from 7.7 g of sodium and 90 ml of absolute alcohol) was heated for five hours. The alcohol was distilled off, water was added to the residue, and the oil that separated was extracted with benzene. Distillation of the reaction products yielded a small amount of the ethyl ester of 4-pentenoic acid and 42.1 g of ethyl 5-ethoxyvalerate, b.p. 87-88° (10 mm); n_D^{20} 1.4225; d_4^{20} 0.9386; found MR 47.16; calculated MR 47.06.

Found %: C 62.15; 62.24; H 10.48; 10.51

$C_9H_{18}O_3$. Calculated %: C 62.07; H 10.34

Ethyl 7-Ethoxyheptanoate. Heating of 48 g of ethyl 7-chloroheptanoate with sodium ethoxide (obtained from 6.3 g of sodium and 80 ml of absolute ethanol) for five hours yielded 45.3 g of ethyl 7-ethoxyheptanoate, b.p. 77-78° (1.5 mm); n_D^{20} 1.4292; d_4^{20} 0.9290; found MR 56.36; calculated MR 56.30.

Found %: C 65.21; 65.18; H 10.81; 10.96

$C_{11}H_{22}O_3$. Calculated %: C 65.34; H 10.89

Triethyl 1,1,5-Pentanetricarboxylate. A mixture of 45 g of ethyl 5-chlorovalerate, sodiomalonic ester (obtained from 70 g of malonic ester and 7.5 g of sodium), 10 g of sodium iodide, and 90 ml of absolute alcohol was heated for six hours. The alcohol was distilled off, water was added to the residue, and the oil that separated was extracted with benzene. Vacuum distillation yielded 67 g (87%) of triethyl 1,1,5-pentanetricarboxylate, b.p. 147-149° (2 mm); n_D^{20} 1.4389; d_4^{20} 1.0568; found MR 71.65; calculated MR 71.81.

Found %: C 58.48; 58.53; H 8.17; 8.22

$C_{14}H_{24}O_6$ Calculated %: C 58.33; H 8.33

A mixture of 60 g of the tricarboxylic ester and 400 ml of hydrochloric acid (1 : 1) was boiled for four hours. The hydrochloric acid was distilled off under reduced pressure, and the residue was heated at 180-190° until evolution of carbon dioxide ceased (30 minutes). The product was 31.2 g of pimelic acid, m.p. 103-104°.

Triethyl 1,1,7-Heptanetricarboxylate. A mixture of 20 g of ethyl 7-chloroheptanoate, sodiomalonic ester (obtained from 32 g of malonic ester and 2.6 g of sodium), 5 g of sodium iodide, and 50 ml of absolute alcohol was heated for ten hours. The product was 25.2 g (79%) of triethyl 1,1,7-heptanetricarboxylate, b.p. 169-170° (1.5 mm); n_D^{20} 1.4419; d_4^{20} 1.0316; found MR 81.03; calculated MR 81.04.

Found %: C 60.92; 60.98; H 8.89; 8.83

$C_{16}H_{28}O_6$ Calculated %: C 60.76 H 8.86

Hydrolysis of the tricarboxylic ester with diluted hydrochloric acid gave azelaic acid in good yield.

9-Phenoxynonanoic Acid. A solution of 10 g of 9-chlorononanoic acid, 10 g of phenol, and 7 g of caustic soda in 40 ml of water was refluxed for three hours. The solution was cooled, filtered, and acidified with hydrochloric acid. The precipitate that formed was filtered off and washed carefully with water. The product was 11.8 g (91%) of 9-phenoxynonanoic acid, m.p. 69-70° (from aqueous methanol).

Found %: C 72.15; 72.18; H 8.98; 8.79

$C_{15}H_{22}O_3$ Calculated %: C 72.00 H 8.80

7-Phenoxyheptanoic Acid. A solution of 10 g of 7-chloroheptanoic acid, 11.5 g of phenol, and 7.2 g of caustic soda in 40 ml of water was heated for five hours. The product was 10.2 g of 7-phenoxyheptanoic acid, m.p. 56-57°

5-Phenoxyvaleric Acid. A mixture of 20 g of δ-valerolactone and sodium phenoxide prepared from 20 g of phenol was heated at 200-210° for 4 hours 30 minutes. The melt was cooled and dissolved in water, and the resulting solution was acidified with hydrochloric acid. The precipitate that formed was filtered off and washed with water. The product was 29.5 g (81%) of 5-phenoxyvaleric acid, m.p. 65-66°.

5-(Phenylthio)valeric Acid. A solution of 10 g of 5-chlorovaleric acid and 3 g of caustic soda in 10 ml of water was mixed with a solution of 10 g of benzenethiol and 3.8 g of caustic soda in 15 ml of water; heat was evolved when the solutions were mixed. The mixture was boiled for two hours, cooled, and acidified with hydrochloric acid. Benzenethiol was steam-distilled off. The product was 10.2 g (65%) of 5-(phenylthio)valeric acid, m.p. 63-64° (from benzene-ligroin) (the literature [12] gives 57°).

Found %: C 62.76; 62.57; H 6.34; 6.31; S 15.04; 15.10

$C_{11}H_{14}O_2$. Calculated %: C 62.80 H 6.56 S 15.21

7-Cyanoheptanoic Acid. A solution was prepared from 16.5 g of 7-chloroheptanoic acid, 4 g of caustic soda, and 30 ml of water. A solution of 8 g of sodium cyanide in 20 ml of water was added, and the mixture was heated at 95-100° for 90 minutes. When the mixture was cool, hydrochloric acid was added, and the oil that separated was extracted with benzene. Vacuum distillation yielded 9.8 g (63%) of 7-cyanoheptanoic acid, b.p. 145-147° (1.5 mm) and m.p. 39-40° (from a mixture of petroleum ether and benzene).

Found %: N 9.09; 9.06

$C_8H_{13}NO_2$. Calculated %: N 9.05

8-Aminooctanoic Acid. 7-Cyanoheptanoic acid (10 g) was dissolved in 30 ml of 25% ammonia and hydrogenated at 65-70° and 90 atm in presence of Raney nickel for two hours. The solution was filtered from the catalyst and evaporated down to remove ammonia. It was then diluted to 50 ml with water, and hydrogen sulfide was passed in order to precipitate nickel. Nickel sulfide was filtered off, and the filtrate was decolorized by treatment with charcoal at the boil. It was evaporated down on a water bath until crystallization began, and ethanol was then added. The mixture was cooled, and the precipitate that formed was filtered off and washed with alcohol. The product was 9.2 g of 8-aminooctanoic acid, m.p. 187-188° (from water) (the literature [13] gives 172°).

Found %: N 8.71; 8.70

$C_8H_{17}NO_2$. Calculated %: N 8.81

7-Hydroxyheptanoic Acid. A solution of 82 g of 7-chloroheptanoic acid and 21 g of caustic soda in 150 ml of water was mixed with a solution of 53 g of sodium carbonate in 250 ml of water. The solution was heated for three hours in an autoclave at 140-150°, cooled, and filtered from insoluble material (4 g, probably polymer of 7-hydroxyheptanoic acid, since it yielded 7-hydroxyheptanoic acid when heated with alkali). It was then acidified with the calculated amount of dilute sulfuric acid. The oil that separated was extracted with ether, and the ether extract was dried with magnesium sulfate. Removal of ether yielded 62.3 g of 7-hydroxyheptanoic acid in the form of a sirup. Oxidation of this substance with nitric acid (sp. gr. 1.40-1.42) resulted in the formation of pimelic acid in good yield.

6-Heptenoic Acid. A solution of 18 g of 7-chloroheptanoic acid, 13.5 g of caustic soda, and 23 g of trimethylamine hydrochloride in 100 ml of water was heated for three hours at 130-140° in an autoclave. The solution was evaporated down to three-quarters of its original volume, 28 g of caustic soda was added, and the mixture was heated in a copper dish with stirring, first at 130-140°, and then at 160-185°, until evolution of trimethylamine ceased (one hour). From time to time small amounts of water were added to replace loss by evaporation. The hot mixture was diluted with water, cooled, and acidified with dilute sulfuric acid. The oil that separated was extracted with ether, and the extract was dried with calcium chloride. Vacuum distillation yielded 10.1 g of 6-heptenoic acid, b.p. 118-120° (14 mm), n_D^{20} 1.4400; and d_4^{20} 0.9500. Its p-toluidide melted at 60-61°. Data in the literature: 6-heptenoic acid n_D^{17} 1.4425 and d_4^{17} 0.952; p-toluidide m.p. 59.6° [14]. Its amide melted at 83-84° (from water).

Found %: N 9.15; 9.21

$C_7H_{13}NO$. Calculated %: N 9.06

5-Chlorovalerophenone. Aluminum chloride (28 g) was added gradually with cooling to a solution of 31 g of 5-chlorovaleryl chloride in 40 ml of benzene. There was rise in temperature, hydrogen chloride was evolved, and the aluminum chloride dissolved. When the whole of the aluminum chloride had been added, the solution was set aside for one hour. It was then boiled for five minutes, cooled, and poured onto ice. The benzene layer was separated and washed with water. After removal of solvent the residue crystallized out. The product was 35.4 g (90%) of 5-chlorovalerophenone, m.p. 49-50° (from alcohol) (the literature [15] gives 51°).

7-Chloroheptanophenone. Aluminum chloride (8.3 g) was added gradually with cooling to a solution of 11 g of 7-chloroheptanoyl chloride in 12 ml of benzene. The mixture was set aside for one hour and then poured onto ice. The product was 9.5 g (72%) of 7-chloroheptanophenone, b.p. 147-148° (1.5 mm) and m.p. 34-35° (from methanol).

Found %: C 69.32; 69.29; H 7.68; 7.52

$C_{13}H_{17}ClO$. Calculated %: C 69.48; H 7.57

Its 2,4-dinitrophenylhydrazone melted at 110-111° (from acetic acid).

Found %: N 12.82; 12.86

$C_{21}H_{25}ClN_4O_4$. Calculated %: N 12.94

5-Phenylvaleric Acid. Aluminum chloride (28 g) was added gradually to a solution of 25 g of 5-chlorovaleric acid in 75 ml of benzene. The solution was heated for one hour in a water bath, cooled, and poured into a mixture of ice and hydrochloric acid. The benzene solution was washed with water and dried with calcium chloride. The residue remaining after removal of solvent was vacuum-distilled, and yielded 26.5 g (80%) of 5-phenylvaleric acid, b.p. 132-133° (1.5 mm) and m.p. 59-60°.

When 20 g of 5-chlorovaleric acid reacted with 65 ml of benzene in presence of 40 g of aluminum chloride under similar conditions, the products were 14.1 g of 5-phenylvaleric acid and 5.5 g of 1-benzosuberanone, b.p. 124-125° (7 mm), n_D^{25} 1.5618; d_4^{25} 1.0780. The dinitrophenylhydrazone melted at 171-172°.

"Phenylheptanoic Acid". Aluminum chloride (18 g) was added gradually to a solution of 20 g of 7-chloroheptanoic acid in 70 ml of benzene. After being heated for 35 minutes, the solution was cooled and poured into a mixture of ice and hydrochloric acid. The benzene solution was washed with water and dried with calcium chloride. The product was 19.1 g (76.5%) of "phenylheptanoic acid", b.p. 165-166° (3 mm); n_D^{20} 1.5089; d_4^{20} 1.0206; found MR 60.26; calculated MR 60.17.

Found %: C 75.56; 75.52; H 8.91; 8.86

$C_{13}H_{18}O_2$. Calculated %: C 75.72; H 8.73

Its amide melted at 55.5-56.5° (from a mixture of ether and petroleum ether). For the amide of 7-phenylheptanoic acid the literature [8] gives m.p. 89°.

Found %: N 6.68; 6.76

$C_{13}H_{19}NO$. Calculated %: N 6.83

When the "phenylheptanoic acid" was oxidized with chromic anhydride, as described below for "phenylnonanoic acid", acetophenone was obtained.

"Phenylnonanoic Acid". Aluminum chloride (16 g) was added to a solution of 20 g of 9-chlorononanoic acid in 70 ml of benzene, and the resulting solution was heated for 45 minutes in a water bath. The product was 18.3 g of "phenylnonanoic acid", b.p. 155-157° (1 mm); n_D^{20} 1.5043; d_4^{20} 0.9957; found MR 69.62; calculated MR 69.40. For 9-phenylnonanoic acid the literature [9] gives m.p. 29-30°, b.p. 215° (12 mm).

Found %: C 76.84; 76.78; H 9.32; 9.24

$C_{15}H_{22}O_2$. Calculated %: C 76.92; H 9.40

A solution of 12 g of chromic anhydride in 30 ml of glacial acetic acid and 5 ml of water was added to a cooled solution of 10 g of the "phenylnonanoic acid" in 36 ml of glacial acetic acid. The mixture was set aside at room temperature for several days, and was then diluted with water and extracted with chloroform. The extract was dried with magnesium sulfate. Vacuum distillation yielded about 1.2 g of a low-boiling fraction and 4.1 g of unchanged "phenylnonanoic acid". Treatment of the low-boiling fraction with 2,4-dinitrophenylhydrazine yielded the 2,4-dinitrophenylhydrazone of acetophenone, m.p. 237-238° (from acetic acid) (in admixture with an authentic sample it melted at 237-238°). Also, by treatment with hydroxylamine, acetophenone oxime was obtained, m.p. 58-59° (in admixture with an authentic sample it melted at 58-59°).

"Phenylundecanoic Acid". A mixture of 11 g of 11-chloroundecanoic acid, 60 ml of benzene, and 7.5 g of aluminum chloride yielded 7.9 g of "phenylundecanoic acid", b.p. 186-188° (3 mm); n_D^{20} 1.5005; d_4^{20} 0.9779; found MR 78.87; calculated MR 78.65.

	Found %:	C 77.93; 78.02;	H 9.94; 9.94
$C_{17}H_{26}O_2$.	Calculated %:	C 77.92	H 9.93

SUMMARY

1. 11-Chlorodecanoic, 13-chlorotridecanoic, and 15-chloropentadecanoic acids have been prepared by hydrolysis of the corresponding $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes.

2. The reactivities of some ω-chloro carboxylic acids have been studied.

3. It has been shown that the condensation of 5-chlorovaleric acid with benzene in presence of aluminum chloride proceeds without isomerization, but that isomerization occurs in the corresponding condensations of 7-chloroheptanoic, 9-chlorononanoic, and 11-chloroundecanoic acids.

4. In order to characterize the ω-chloro carboxylic acids studied, some of their derivatives have been prepared.

LITERATURE CITED

[1] R. Joyce, W. Hanford, J. Harmon, J. Am. Chem. Soc. 70, 2529 (1948).

[2] W. Hanford, R. Joyce, U. S. Pat. 2440800, CA 42, 6373 (1948).

[3] R. Joyce, U. S. Pat. 2398430, CA 40, 3768 (1946).

[4] A. N. Nesmeyanov, L. I. Zakharkin, and P. G. Petrova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 2, 253.*

[5] German Pat. 741687, C. 1944, 1, 907.

[6] I. Eykmann, Chem. Weekblad 4, 727 (1907).

[7] R. Christian, J. Am. Chem. Soc. 74, 1591 (1952).

[8] J. v. Braun, Ber. 44, 2878 (1911).

[9] H. G. Raper, E. J. Wayne, Biochem. J. 22, 194 (1928).

[10] E. Fourneau, P. Baranger, Bull. Soc. Chim. 49, 1161 (1931).

[11] E. Abraham, J. Smith, J. Chem. Soc. 1936, 1605.

[12] P. Cagniaut, A. Deluzarche, Comptes rend., 223, 677 (1946).

[13] A. Geldsobel, Ber. 27, 3128 (1894).

[14] O. Wallach, Ann. 312, 207 (1900), P. Gaubert, R. Linstead, H. Rydon, J. Chem. Soc. 1937, 1971.

[15] H. Normant, Comptes rend., 231, 909 (1950).

Received April 20, 1954

Institute of Heteroorganic Compounds of the
USSR Academy of Sciences

---

* See Consultants Bureau Translation, p. 205.

BLANK
PAGE

CHLORINATION AND DEHYDROCHLORINATION OF POLYCHLORO COMPOUNDS CONTAINING REACTIVE GROUPS

R. Kh. Freidlina, V. N. Kost, and A. N. Nesmeyanov

The reaction of chlorine with unsaturated hydrocarbons is a very complex process. Chlorination of olefins may proceed, depending on conditions, by a heterolytic (eletrophilic), or by a homolytic mechanism. Initial and final reaction components, for example those of structure $CH_2{=}\overset{|}{C}-\underset{|}{\overset{|}{C}}-H$ and $CH_2{=}\overset{|}{C}-\underset{|}{\overset{|}{C}}-Cl$, readily undergo isomerization, and the compounds formed initially may react further with chlorine and with hydrogen chloride. Reaction may proceed, therefore, in various directions, and among the most important of these are the formation of saturated addition products and the formation of unsaturated chloro olefins by "allyl chlorination". By "allyl chlorination" we mean replacement of hydrogen attached to a carbon atom adjacent to a double bond, the position of the entering chlorine atom being determined by the mechanism of the reaction.

Branched unsaturated hydrocarbons having a tertiary carbon at the double bond react with chlorine even at room temperature with formation of chloro olefins, as was noted for the first time by Lvov and Sheshukov [1]. This important reaction was subsequently investigated by several Russian workers, including Kondakov, Pogorzhelsky, Ostromyslensky, and Tishchenko.

Normal olefins behave differently. At low temperatures they unite with chlorine at the double bond, and at high temperatures (300-600° for propene) they undergo allyl chlorination with formation of chloro olefins [2]. For 1,2-disubstituted ethylenes cases are known in which reaction with chlorine at slightly above room temperature results in the formation of small amounts of chloro olefins, as well as addition products. For example, when chlorine reacted with 2-pentene in a hot carbon tetrachloride medium, a small amount of 1-chloro-2-pentene was isolated, as well as the addition product [3].

This paper describes a study of the reaction of chlorine with compounds containing the 2,2-dichlorovinyl group (or substituted 2,2-dichlorovinyl group) and also the dehydrochlorination of the resulting polychloro compounds. Since compounds of structure $CCl_2{=}\overset{|}{C}-\underset{|}{\overset{|}{C}}-Cl$, unlike those of structure $CH_2{=}\overset{|}{C}-\underset{|}{\overset{|}{C}}-Cl$, are inert to anionotropic allyl rearrangement [4], it may be expected that the analysis of their behavior in chlorination will be rather simpler.

We have studied the action of chlorine on compounds of structure:

$$CCl_2{=}CX-CH_2Y,$$

$(X = H, Cl; Y = C_6H_5, OCH_3, N(C_2H_5)_2, NO_2)$.

In these compounds the readiness with which the allyl hydrogen atoms are replaced by chlorine should depend on the nature of the substituent attached to the methylene group. The chlorination was carried out under mild conditions in carbon tetrachloride, usually with cooling. For the less reactive substances heating was applied and the reaction mixture was illuminated with a 150-watt filament lamp.

The compounds can be divided into two groups, according to their behavior towards chlorine. The first group includes:

$$CCl_2{=}CH-CH_2C_6H_5,\ CCl_2{=}CCl-CH_2C_6H_5,\ CCl_2{=}CH-CH_2-NO_2,$$

to which chlorine adds smoothly according to the equation

$$CCl_2{=}CXCH_2Y + Cl_2 \longrightarrow CCl_3CXClCH_2Y. \qquad (1)$$

In these cases the evolution of hydrogen chloride, which is associated with the occurrence of allyl chlorination, does not occur to an appreciable extent. The authors of this paper in collaboration with Zakharkin [5] have shown that compounds of structure $CCl_2{=}CH-CH_2-CN$ and $CCl_2{=}CH-CH_2-COOH$ also unite readily with chlorine without yielding appreciable amounts of products of allyl chlorination.

The second group includes compounds of structure:

$$CCl_2{=}CH-CH_2OCH_3,\ CCl_2{=}CCl-CH_2OCH_3,\ CCl_2{=}CHCH_2N(C_2H_5)_2.$$

and even under the mildest conditions at −5° to 0° without irradiation these compounds react with chlorine with copious evolution of hydrogen chloride, indicating the occurrence of allyl chlorination. The main reaction is

$$CCl_2{=}CX{-}CH_2Y + 2Cl_2 \longrightarrow CCl_3CXClCHClY + HCl. \qquad (2)$$

These results show that in compounds of structure $CCl_2{=}CX{-}CH_2Y$, in which the methylene group is attached to an electron-accepting substituent, the replacement of hydrogen by chlorine is difficult, whereas in the compounds in which the methylene group is attached to an electron-donating substituent, the replacement of hydrogen by chlorine is facilitated. This conclusion is confirmed by the fact that when compounds of the second group react with chlorine in a hydrochloric acid medium allyl chlorination (Equation 2) begins to play a subordinate role and the reaction proceeds mainly according to Equation 1. This effect is clearly associated with the conversion of the electron-donating group into an electron acceptor under these conditions, as indicated in the schemes:

$$CCl_2{=}CX{-}CH_2OCH_3 + HCl \rightleftharpoons [CCl_2{=}CH{-}CH_2\overset{+}{O}(H){-}CH_3]Cl^{-}$$

$$CCl_2{=}CH{-}CH_2N(C_2H_5)_2 + HCl \rightleftharpoons [CCl_2{=}CH{-}CH_2\overset{+}{N}H(C_2H_5)_2]Cl^{-}.$$

It is known also that diallyl ether [6], allyl alcohol, allyl acetate, and allyl benzoate [7] unite smoothly with chlorine in a hydrochloric acid medium.

The tetrachloro compounds that we obtained, namely

$$CCl_3CHClCH_2Y\ [Y{=}C_6H_5,\ OCH_3,\ N(C_2H_5)_2]$$

were subjected to dehydrochlorination with alcoholic potash with the object of determining the effect of the nature of the substituent attached to the methylene group on the direction in which hydrogen chloride was eliminated from these molecules.

In all of these cases elimination was in accord with Zaitsev's rule, i.e.

$$CCl_3{-}CHCl{-}CH_2Y \xrightarrow{KOH} CCl_2{=}CCl{-}CH_2Y.$$

We have previously shown, in collaboration with Zakharkin [5], that the dehydrochlorination of compounds of structure $CCl_3CHClCH_2CN$ and $CCl_3CHClCH_2COOH$ in presence of alcoholic potash proceeds in the direction contrary to Zaitsev's rule, i.e.

$$CCl_3{-}CHCl{-}CH_2Y \xrightarrow{KOH} CCl_3{-}CH{=}CHY.$$

The observations now described show that in the dehydrochlorination of compounds of structure $CCl_3{-}CHCl{-}CH_2Y$ reaction is in accord with Zaitsev's rule when Y is an electron donor, but when it is a strong electron acceptor the reaction is contrary to Zaitsev's rule.

The phenyl group was found to have opposite effects in the chlorination and dehydrochlorination reactions.

The methods of preparing the compounds studied and of establishing their structures will be clear from the following schemes.

For substances containing the phenyl group:

$$\underset{(I)}{CCl_2{=}CH{-}CH_2C_6H_5} \xrightarrow{Cl_2} \underset{(II)}{CCl_3CHClCH_2C_6H_5} \xrightarrow{KOH}$$

$$\longrightarrow \underset{(III)}{CCl_2{=}CCl{-}CH_2C_6H_5} \xrightarrow{Cl_2} \underset{(IV)}{CCl_3CCl_2CH_2C_6H_5}.$$

Compound (I) was prepared as already described [4]. Compound (IV) was identified with (2,2,3,3,3-pentachloropropyl) benzene as prepared by the reactions

$$CCl_2{=}CCl{-}CH_2Cl + C_6H_6 \xrightarrow{AlCl_3} CCl_2{=}CCl{-}CH_2C_6H_5 \xrightarrow{Cl_2} CCl_3CCl_2CH_2C_6H_5,$$

by means of a mixture melting point.

For substances containing a methoxyl group:

$$\underset{(V)}{CCl_2{=}CH{-}CH_2OCH_3} \xrightarrow[HCl]{Cl_2} \underset{(VI)}{CCl_3CHClCH_2OCH_3} \xrightarrow{KOH} \underset{(VII)}{CCl_2{=}CCl{-}CH_2OCH_3} \xrightarrow[HCl]{Cl_2} CCl_3CCl_2CH_2OCH_3;$$

compound (V) was prepared as previously described [8]. Compound (VII) was found to have constants identical with those of the substance synthesized by the reaction:

$$CCl_2{=}CClCH_2Cl + CH_3ONa \longrightarrow CCl_2{=}CClCH_2OCH_3.$$

For compounds containing the diethylamino group:

$$\underset{(VIII)}{CCl_2{=}CH{-}CH_2N(C_2H_5)_2} \xrightarrow[HCl]{Cl_2} CCl_3CHClCH_2N(C_2H_5)_2 \cdot HCl \xrightarrow{KOH} CCl_2{=}CCl{-}CH_2N(C_2H_5)_2 \xrightarrow{HCl}$$

$$\longrightarrow \underset{(IX)}{CCl_2{=}CClCH_2N(C_2H_5)_2 \cdot HCl}.$$

Compound (VIII) was prepared as previously described [8]. Compound (IX) was identified with the substance prepared by the reaction:

$$CCl_2{=}CClCH_2Cl + (C_2H_5)_2NH \longrightarrow CCl_2{=}CClCH_2N(C_2H_5)_2 \cdot HCl,$$

by making a mixture melting point test on hydrochlorides prepared by the two methods.

For compounds containing the nitro group:

$$CCl_2{=}CH{-}CH_2Cl + AgNO_2 \longrightarrow CCl_2{=}CHCH_2NO_2 \xrightarrow{Cl_2} CCl_3CHClCH_2NO_2.$$

The tetrachloronitropropane prepared by these reactions had constants that differed from those of the substance originally described as 1,1,1,2-tetrachloro-3-nitropropane, which was synthesized by the action of phosphorus pentachloride on 1,1,1-trichloro-3-nitro-2-propanol. It has since been shown [11] that the compound prepared by the latter method is actually 3,3,3-trichloro-1-nitropropene, and our findings are in agreement with this result.

EXPERIMENTAL

Action of Chlorine on (3,3-Dichloroallyl) benzene

Chlorine was passed at 60° through a solution of 40 g of (3,3-dichloroallyl) benzene in 50 ml of carbon tetrachloride until a state of saturation was attained. The solvent was distilled off, and the residue was vacuum-distilled. A fraction boiling at 130-140° (7 mm) was collected. Redistillation yielded 45 g (82%) of (2,3,3,3-tetrachloropropyl)-benzene, b.p. 111-112° (2 mm); n_D^{20} 1.5535; d_4^{20} 1.3867; found MR 59.58; calculated for $C_9H_8Cl_4\,3\Gamma$ MR 59.63.

Found %: C 42.43; 42.36; H 3.18; 3.20

$C_9H_8Cl_4$. Calculated %: C 41.90; H 3.12

Dehydrochlorination of (2,3,3,3-Tetrachloropropyl)benzene

A solution of 10 g (0.18 mole) of caustic potash in 50 ml of alcohol was added dropwise to a stirred solution of 38 g (0.17 mole) of (2,3,3,3-tetrachloropropyl)benzene. The mixture was left overnight at room temperature. The reaction product was precipitated with water, separated, washed, and dried over calcium chloride. Distillation yielded 25 g (80%) of (2,3,3-trichloroallyl)benzene, b.p. 121-122° (8 mm); n_D^{20} 1.5622; d_4^{20} 1.3230; found MR 54.34; calculated for $C_9H_7Cl_3\Gamma_4$ MR 54.29. The constants given in the paper of Nesmeyanov, Freidlina, and Firstov [4] were b.p. 121-122° (8 mm); n_D^{20} 1.5630; d_4^{20} 1.3232.

By the action of chlorine on this compound a good yield of crystalline (2,2,3,3,3-pentachloropropyl)benzene, m.p. 76-77°, was obtained.

Found %: C 37.11; 37.18; H 2.42; 2.54

$C_9H_7Cl_5$. Calculated %: C 36.96; H 2.41

This pentachloro compound gave no melting point depression in admixture with the pentachloro compound obtained by the action of chlorine on the (2,3,3-trichloroallyl)benzene obtained by the condensation of benzene with 1,1,2,3-tetrachloropropene [4].

Action of Chlorine on 3,3-Dichloroallyl Methyl Ether

a) Reaction in Chloroform Solution. When the reaction was carried out in chloroform solution at −5° to 0°, copious evolution of hydrogen chloride was observed. A mixture of chlorination products was obtained, and from this a pentachloro compound was isolated in 62% yield. It boiled at 97-98° (5.5 mm) and had n_D^{20} 1.5098; d_4^{20} 1.5740; it has been described previously [8]. No methyl tetrachloropropyl ether was obtained.

b) Reaction in presence of Hydrogen Chloride. A mixture of 28 g (0.15 mole) of 3,3-dichloroallyl methyl ether, 20 ml of diethyl ether, and 15 ml of concentrated hydrochloric acid was saturated with hydrogen chloride at −5°, and chlorine mixed with hydrogen chloride was then passed through the mixture at −5 to 0° until saturation with chlorine was attained. The mixture was diluted with water, and the organic layer was separated, washed with a 3% solution of sodium carbonate and with water, and dried over calcium chloride. Distillation yielded 19.5 g (61%) of methyl 2,3,3,3-tetrachloropropyl ether b. p. 58.5-59° (4 mm); n_D^{20} 1.4868; d_4^{20} 1.4568; found MR 41.82; calculated for $C_4H_6Cl_4O$ MR 41.78.

Found %: C 22.96; 22.94; H 2.89, 2.88; Cl 67.01; 67.27

$C_4H_6Cl_4O$. Calculated %: C 22.66; H 2.85; Cl 66.93

Dehydrochlorination of Methyl 2,3,3,3-Tetrachloropropyl Ether

A solution of 4.5 g of caustic potash in 25 ml of methanol was added a little at a time to 14 g of methyl 2,3,3,3-tetrachloropropyl ether. The mixture was set aside overnight. The mixture was diluted with water, and the lower layer was separated, washed with water, dried over calcium chloride. Distillation yielded 10.3 g (90%) of methyl 2,3,3-trichloroallyl ether, b.p. 53-54° (10 mm); n_D^{20} 1.4871; d_4^{20} 1.3782; found MR 36.62; calculated for $C_4H_5Cl_3O$ F MR 36.45.

Found %: C 27.29; 27.26; H 2.70, 2.61

$C_4H_5Cl_3O$ Calculated %: C 27.38; H 2.87

The constants of this compound are in good agreement with the constants of methyl 2,3,3-trichloroallyl ether prepared in the following manner: 1,1,2,3-tetrachloropropene (50 g) was heated for eight hours with a solution of sodium methoxide prepared from 7 g of sodium and 80 ml of methanol. The mixture was diluted with water, and the organic layer was separated, washed with water, and dried over calcium chloride. Distillation yielded 36 g (72%) of methyl 2,3,3-trichloroallyl ether boiling at 54° (10 mm) and having n_D^{20} 1.4875; d_4^{20} 1.3794. The same methyl trichloroallyl ether was obtained by the action of sodium methoxide on 2,3,3,3-tetrachloropropene.

Action of Chlorine on Methyl 2,3,3-Trichloroallyl Ether

a) It was found that a chloroform solution of methyl 2,3,3-trichloroallyl ether does not react, or reacts only very slowly, with chlorine at 0°. When the solution is heated or irradiated reaction proceeds with evolution of hydrogen chloride. For example, when chlorine was passed through a solution of 9 g of methyl 2,3,3-trichloroallyl ether in chloroform maintained at −5° to 0° and irradiated by a 100-watt lamp, a mixture of chlorination products was obtained. This boiled at 89-107° (3 mm) and had n_D^{20} 1.5261–1.5309; d_4^{20} 1.6930 – 1.7227.

b) When the reaction was carried out in presence of hydrogen chloride, the main reaction product was a pentachloro compound. A solution of 8 g of methyl 2,3,3-trichloroallyl ether in 15 ml of concentrated hydrochloric acid was saturated with hydrogen chloride at −5°, and at this temperature, under the illumination of a 150-watt lamp, chlorine and hydrogen chloride were passed for five hours. The mixture was then diluted with water, and the reaction product was extracted with chloroform. The chloroform extract was washed with a 3% solution of sodium carbonate and with water, and then dried over calcium chloride. The solvent was distilled off, and vacuum distillation of the residue yielded 6 g (50%) of a methyl pentachloropropyl ether, b.p. 63-64° (2 mm); n_D^{20} 1.5085; d_4^{20} 1.5765; found MR 46.62; calculated for $C_4H_5Cl_5O$ MR 46.65.

Found %: C 19.72; 19.82; H 1.87; 2.00

$C_4H_5Cl_5O$. Calculated %: C 19.50; H 2.04

In addition some unchanged methyl 2,3,3-trichloroallyl ether and a small amount of high-boiling fractions were isolated.

Action of Chlorine on 3,3-Dichloro-N,N-diethylallylamine Hydrochloride

The reaction was carried out in concentrated hydrochloric acid saturated with hydrogen chloride at 0°. Reaction did not go in the dark (after chlorine had been passed for five hours the original compound was recovered unchanged). When the mixture was irradiated by a 150-watt lamp at 0 - 5°, 10 g of 3,3-dichloro-N,N-diethylallylamine hydrochloride yielded 12 g (85%) of 2,3,3,3-tetrachloro-N,N-diethylpropylamine hydrochloride, m.p. 180-181° (from absolute alcohol).

Found %: C 29.16; 29.07; H 4.94; 4.87

$C_7H_{14}Cl_5N$. Calculated %: C 29.04; H 4.87

When the reaction between chlorine and the free base [$CCl_2{=}CH-CH_2N(C_2H_5)_2$] was carried out in chloroform with cooling, a mixture of hydrochlorides was formed, and these were not investigated further.

Dehydrochlorination of 2,3,3,3-Tetrachloro-N,N-diethylpropylamine

A solution of 1.5 g (0.026 mole) of caustic potash in 10 ml of methanol was added to a solution of 3.5 g (0.012 mole) of 2,3,3,3-tetrachloro-N,N-diethylpropylamine hydrochloride in 10 ml of methanol. The mixture was left at room temperature overnight, and then diluted with water and extracted with chloroform. The chloroform extract was washed with water and dried over potassium carbonate. The solvent was distilled off, and vacuum distillation of the residue then yielded 1.5 g (60%) of 2,3,3-trichloro-N,N-diethylallylamine, b.p. 81-82° (4 mm); n_D^{20} 1.4894; d_4^{20} 1.1942. The hydrochloride melted at 168-169° (from a mixture of benzene and chloroform). A mixture of this with the hydrochloride of the amine prepared by reaction of 1,1,2,3-tetrachloropropene with diethylamine melted at 168-169°.

Preparation of 2,3,3-Trichloro-N,N-diethylallylamine

A solution of 18 g of 1,1,2,3-tetrachloropropene and 14 g of diethylamine in 40 ml of methanol was heated in a water bath for eight hours. Methanol was distilled off, and the residue was dissolved in dilute hydrochloric acid. The solution was extracted with ether and then made alkaline with 10% caustic potash. The amine that separated was extracted with chloroform, and the chloroform extract was washed with water and dried over potassium carbonate. Distillation yielded 17.8 g (82%) of 2,3,3-trichloro-N,N-diethylallylamine, b.p. 72° (3 mm); n_D^{20} 1.4888; d_4^{20} 1.1922; found MR 52.40; calculated for $C_7H_{12}Cl_3N\Gamma$ MR 52.60. Its hydrochloride melted at 168-169°.

Found %: N 5.45; 5.37

$C_7H_{12}Cl_3N$. Calculated %: N 5.53

Preparation of 1,1-Dichloro-3-nitropropene

Silver nitrate (13 g) was added a little at a time to 20 g of 1,1,3-trichloropropene. The mixture was heated in a water bath for one hour. The reaction product was extracted with ether. The ether was distilled off, and vacuum distillation of the residue yielded 3.1 g of 1,1-dichloro-3-nitropropene, b.p. 47-48° (2 mm); n_D^{20} 1.4879; d_4^{20} 1.4494; found MR 31.00; calculated for $C_3H_3Cl_2NO_2\Gamma$ MR 30.95

Found %: C 23.11; 23.32; H 2.16; 2.11

$C_3H_3Cl_2NO_2$. Calculated %: C 23.10; H 1.94

Action of Chlorine on 1,1-Dichloro-3-nitropropene

Chlorine was passed for five hours through a boiling solution of 2.3 g of 1,1-dichloro-3-nitropropene that was under the illumination of a 150-watt lamp. The solvent was distilled off, and vacuum distillation of the residue yielded 2.1 g (70%) of a tetrachloronitropropane of boiling point 73-74° (1.5 mm); it had n_D^{20} 1.5005; d_4^{20} 1.6355; found MR 40.84; calculated for $C_3H_3Cl_4NO_2$ MR 41.14.

Found %: C 15.72; 15.81; H 1.34; 1.39

$C_3H_3Cl_4NO_2$. Calculated %: C 15.88; H 1.33

SUMMARY

1. It has been found that compounds of structure $CCl_2=CX-CH_2Y$ ($X = H, Cl$; $Y = C_6H_5, OCH_3, N(C_2H_5)_2, NO_2$) unite smoothly with chlorine at the double bond when the substituent at the methylene group is electron-accepting, but when this substituent is an electron donor allyl chlorination occurs.

2. When the substance of structure $CCl_2=CX-CH_2Y$ contains an electron-donating substituent at the methylene group (e.g. OCH_3, $N(C_2H_5)_2$) and is capable of being converted into an onium compound in an acid medium, allyl chlorination can be suppressed by carrying out the chlorination in a hydrochloric acid medium.

3. In the dehydrochlorination of compounds of structure $CCl_3CHClCH_2Y$ by means of alcoholic caustic potash, when the substituent is an electron-donating group (e.g. OCH_3, $N(C_2H_5)_2$) the process is in the direction required by Zaitsev's rule, and when it is an electron-accepting group (e.g. CN, COOH) the process is contrary to Zaitsev's rule.

4. In the chlorination of $CCl_2=CXCH_2C_6H_5$ the effect of the phenyl group is similar to that of the electron-accepting groups. The dehydrochlorination of $CCl_3CHClCH_2C_6H_5$ proceeds in the direction required by Zaitsev's rule.

Received June 3, 1954

Institute of Heteroorganic Compounds of the
USSR Academy of Sciences

LITERATURE CITED

[1] M. D. Lvov, J. Russ. Phys. Chem. Soc., 16, 462 (1884); 17, 301 (1885); M. I. Sheshukov, J. Russ. Phys. Chem. Soc., 16, 478 (1884).

[2] H. Groll, G. Hearn, Ind. Eng. Chem. 31, 1530 (1939).

[3] T. Stewart, B. Weidenbaum, J. Am. Chem. Soc. 58, 98 (1936).

[4] A. N. Nesmeyanov, R. Kh. Freidlina, and V. I. Firstov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1951, 503; Proc. Acad. Sci. USSR, 78, 717 (1951).

[5] A. N. Nesmeyanov, L. I. Zakharkin, V. N. Kost, and R. Kh. Freidlina, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 2, 258. *

[6] U. S. Pat. 2464758. C. A. 43, 4682 (1949).

[7] H. Ing, J. Chem. Soc. 1948, 1393.

[8] A. N. Nesmeyanov, L. I. Zakharkin, V. N. Kost, and R. Kh. Freidlina, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 4, 604. **

[9] L. Henry, Bull. Acad. roy. méd. Belg. 34, 568 (1897).

[10] H. Irving, J. Chem. Soc. 1936, 797.

[11] F. Brower, H. Burkett, J. Am. Chem. Soc. 75, 1082 (1953).

---

*See Consultants Bureau Translation, p. 209.

** " " " " p. 515.

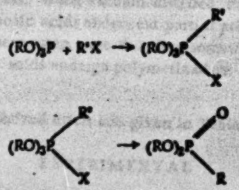
DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 5. ESTERS OF 2-ETHOXY-, 2-PROPOXY-, 2-BUTOXY-, AND 2-HEXYLOXY-VINYLPHOSPHONIC ACIDS

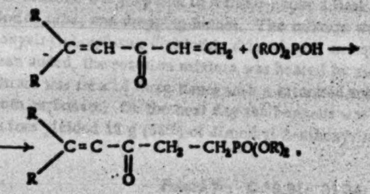
K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov

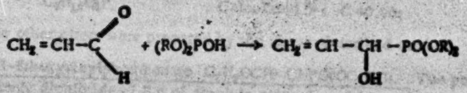
In our first communication we described a simple, convenient method for the preparation of the previously unknown 2-alkoxyvinylphosphonic dichlorides [1]. Starting from these acid chlorides we have prepared various esters, amides, thio esters, and other derivatives of 2-alkoxyvinylphosphonic acids.

There have been very few investigations on the esters of unsaturated phosphonic acids, and most of these have been carried out by Arbuzov and his students [2 - 10]. They prepared these compounds either with the aid of the Arbuzov isomerization, i.e.,



(R' is an unsaturated radical and X is a halogen), or by the addition of dialkyl hydrogen phosphites to unsaturated ketones and aldehydes in presence of sodium alkoxides, i.e.,

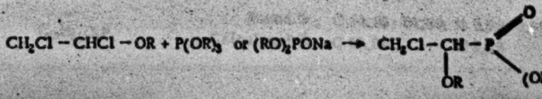


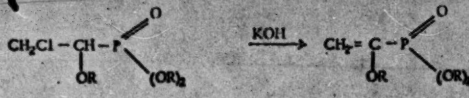


Also, Kabachnik [11] has described the syntheses of the diethyl and bis(2-chloroethyl) esters of vinylphosphonic acid. He obtained these compounds by the elimination of hydrogen chloride from the corresponding esters of 2-chloroethylphosphonic acid with potassium hydroxide solution:

$$Cl-CH_2-CH_2PO(OR)_2 + KOH = CH_2=CHPO(OR)_2 + KCl + H_2O.$$

Pudovik and Denisova [12] have recently described syntheses of the ethyl esters of 1-ethoxy- and 2-butoxy-vinylphosphonic acids. The general scheme of the syntheses was as follows:





Diesters of 2-alkoxyvinylphosphonic acids can be prepared by various methods:

1. Reaction of alcohols with 2-alkoxy (or phenoxy) vinylphosphonic dichlorides in presence of pyridine

$$ROCH=CHPOCl_2 + 2ROH + 2C_5H_5N = ROCH=CHPO(OR)_2 + 2C_5H_5N\cdot HCl.$$

2. Reaction of alcohols with these acid chlorides, cooling being applied

$$RO\cdot CH=CHPOCl_2 + 2ROH = ROCH=CHPO(OR)_2 + 2HCl.$$

3. Reaction of the acid chlorides with sodium alkoxides

$$RO\cdot CH=CHPOCl_2 + 2RONa = ROCH=CHPO(OR)_2 + 2NaCl.$$

4. Reaction of salts of 2-alkoxy (or phenoxy) vinylphosphonic acids with alkyl halides

$$RO\cdot CH=CHPO(ONa)_2 + RX = ROCH=CHPO(OR)_2 + 2NaCl.$$

We used the first method, which is due to Milobendzski and Sachnowski [13]. By this means we have prepared the dimethyl, diethyl, dipropyl, diisopropyl, dibutyl, diisobutyl, diallyl, dihexyl, bis(2-methoxyethyl), and bis(2-ethoxyethyl) esters of 2-ethoxy-, 2-propoxy-, 2-butoxy-, and 2-hexyloxy-vinylphosphonic acids. Yields of up to 80% were obtained. All of the esters are liquids that can be vacuum-distilled without decomposition and are readily soluble in the usual organic solvents. When vacuum-distilled, the diisopropyl esters of 2-ethoxy-, 2-propoxy-, 1-butoxy-, and 2-hexyloxy-vinylphosphonic acids underwent partial polymerization with formation of a thick mass in the distillation flask. The yields of these esters were therefore somewhat lower than those of the other esters. The diallyl esters of 2-alkoxyvinylphosphonic acids undergo polymerization, and will copolymerize with unsaturated compounds, in presence of organic peroxides.

The physical constants of the synthesized esters are given in Table 1-4.

EXPERIMENTAL

Diesters of 2-Ethoxyvinylphosphonic Acid

Dimethyl 2-Ethoxyvinylphosphonate $C_2H_5OCH=CHPO(OCH_3)_2$. A mixture of 7.7 g of absolute methanol, 19.7 g of pyridine, and 100 ml of benzene was prepared in a three-necked flask fitted with stirrer, reflux condenser protected with a calcium chloride tube, and dropping funnel. The mixture was well cooled and stirred while addition was made of 23 g of 2-ethoxyvinylphosphonic dichloride diluted with an equal volume of benzene. When the whole of the acid chloride had been added, the reaction mixture was heated for two hours in a water bath. The precipitate was filtered off, and the filtrate was treated three times with a saturated solution of sodium carbonate. It was then dried with calcined potassium carbonate. On the next day the benzene was driven off and the residue was vacuum-distilled. Three fractionations yielded 13 g (56%) of dimethyl 2-ethoxyvinylphosphonate, b.p. 87° (2mm); d_4^{20} 1.1451; n_D^{20} 1.4508

Found %: C 39.91; 39.84; H 7.44; 7.41
$C_6H_{13}O_4P$. Calculated %: C 40.00; H 7.22

All of the other esters were prepared by the above-described method.

Diethyl 2-Ethoxyvinylphosphonate $C_2H_5OCH=CHPO(OC_2H_5)_2$. The product obtained from 15 g of 2-ethoxyvinylphosphonic dichloride, 7.3 g of absolute ethanol, and 13 g of pyridine was 7.5 g (45%) of a substance having b.p. 99.5-100° (2 mm); d_4^{20} 1.0710; n_D^{20} 1.4476

Found %: C 46.50; 46.48; H 8.82; 8.76
$C_8H_{17}O_4P$. Calculated %: C 46.15; H 8.17

Dipropyl 2-Ethoxyvinylphosphonate $C_2H_5OCH=CHPO(OC_3H_7-n)_2$. 2-Ethoxyvinylphosphonic dichloride (16 g) was added to a solution of 10.15 g of propyl alcohol in 80 ml of benzene, and 14 g (70%) of the ester was isolated. It had b.p. 103° (1.5 mm); d_4^{20} 1.0335; n_D^{20} 1.4475

Found %: C 50.90; 50.99; H 9.09; 9.07
$C_{10}H_{21}O_4P$. Calculated %: C 50.84; H 8.89

TABLE 1

Formula of compound	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}
$C_2H_5-O-CH=CHPO(OCH_3)_2$	87 (2)	1,4508	1,1451
$C_2H_5-O-CH=CHPO(OC_2H_5)_2$	99.5 (2)	1,4476	1,0710
$C_2H_5-O-CH=CHPO(OC_3H_7\text{-}n)_2$	103 (1.5)	1,4475	1,0335
$C_2H_5-O-CH=CHPO(OC_3H_7\text{-}i)_2$	91 (2)	1,4402	1,0171
$C_2H_5-O-CH=CHPO(OC_4H_9\text{-}n)_2$	127 (2)	1,4492	1,0069
$C_2H_5-O-CH=CHPO(OC_4H_9\text{-}i)_2$	107 (0.5)	1,4453	1,0004
$C_2H_5-O-CH=CHPO(OC_6H_5)_2$	112 (1)	1,4698	1,0792
$C_2H_5-O-CH=CHPO(OC_6H_{13}\text{-}n)_2$	157–158 (2)	1,4511	0,9710
$C_2H_5-O-CH=CHPO(OCH_2-CH_2-OCH_3)_2$	155 (2)	1,4568	1,1267
$C_2H_5-O-CH=CHPO(OCH_2-CH_2-OC_2H_5)_2$	158 (1)	1,4545	1,0842

TABLE 2

Formula of compound	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}
$n\text{-}C_3H_7-O-CH=CHPO(OCH_3)_2$	95 (1)	1,4500	1,1095
$n\text{-}C_3H_7-O-CH=CHPO(OC_2H_5)_2$	106 (1)	1,4455	1,0523
$n\text{-}C_3H_7-O-CH=CHPO(OC_3H_7\text{-}n)_2$	128 (2)	1,4471	1,0201
$n\text{-}C_3H_7-O-CH=CHPO(OC_3H_7\text{-}i)_2$	110 (2)	1,4402	1,0042
$n\text{-}C_3H_7-O-CH=CHPO(OC_4H_9\text{-}n)_2$	139 (2)	1,4485	0,9969
$n\text{-}C_3H_7-O-CH=CHPO(OC_4H_9\text{-}i)_2$	121 (2)	1,4449	0,9906
$n\text{-}C_3H_7-O-CH=CHPO(OC_6H_5)_2$	123 (1)	1,4675	1,0557
$n\text{-}C_3H_7-O-CH=CHPO(OC_6H_{13}\text{-}n)_2$	157 (1)	1,4509	0,9664
$n\text{-}C_3H_7-O-CH=CHPO(OCH_2-CH_2-OCH_3)_2$	158 (1)	1,4565	1,1089
$n\text{-}C_3H_7-O-CH=CHPO(OCH_2-CH_2-OC_2H_5)_2$	156 (2)	1,4580	1,0694

TABLE 3

Formula of compound	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}
$n\text{-}C_4H_9-O-CH=CHPO(OCH_3)_2$	111 (2)	1,4515	1,0867
$n\text{-}C_4H_9-O-CH=CHPO(OC_2H_5)_2$	116 (2)	1,4460	1,0360
$n\text{-}C_4H_9-O-CH=CHPO(OC_3H_7\text{-}n)_2$	123 (2)	1,4478	1,0060
$n\text{-}C_4H_9-O-CH=CHPO(OC_3H_7\text{-}i)_2$	105 (2)	1,4401	0,9916
$n\text{-}C_4H_9-O-CH=CHPO(OC_4H_9\text{-}n)_2$	144 (2)	1,4491	0,9879
$n\text{-}C_4H_9-O-CH=CHPO(OC_4H_9\text{-}i)_2$	131.5 (2)	1,4460	0,9810
$n\text{-}C_4H_9-O-CH=CHPO(OC_6H_5)_2$	139.5 (2)	1,4651	1,0442
$n\text{-}C_4H_9-O-CH=CHPO(OC_6H_{13}\text{-}n)_2$	164–165 (2)	1,4518	0,9635
$n\text{-}C_4H_9-O-CH=CHPO(OCH_2-CH_2-OCH_3)_2$	161 (2)	1,4558	1,0873
$n\text{-}C_4H_9-O-CH=CHPO(OCH_2-CH_2-OC_2H_5)_2$	164 (2)	1,4532	1,0584

Diisopropyl 2-Ethoxyvinylphosphonate $C_2H_5OCH{=}CHPO(OC_3H_7\text{-i})_2$. Isopropyl alcohol was substituted for propyl alcohol in the above synthesis, the amounts taken and the reaction conditions being exactly the same. The yield of diisopropyl 2-ethoxyvinylphosphonate was 10 g (50%). It had b.p. 91° (2 mm); d_4^{20} 1.0171; n_D^{20} 1.4402.

Found %: C 51.04; 51.10; H 8.97; 9.10
$C_{10}H_{21}O_4P$. Calculated %: C 50.84; H 8.89

Dibutyl 2-Ethoxyvinylphosphonate $C_2H_5OCH{=}CHPO(OC_4H_9\text{-n})_2$. The product obtained from 14 g of butyl alcohol, 15.81 g of pyridine, and 18.9 g of 2-ethoxyvinylphosphonic dichloride was 20 g (75%) of dibutyl 2-ethoxyvinylphosphonate, b.p. 127° (2 mm); d_4^{20} 1.0069; n_D^{20} 1.4492.

Found %: C 54.80; 54.78; H 9.70; 9.49
$C_{12}H_{25}O_4P$. Calculated %: C 54.54; H 9.46

Diisobutyl 2-Ethoxyvinylphosphonate $C_2H_5OCH{=}CHPO(OC_4H_9\text{-i})_2$. The product obtained from 14.81 g of isobutyl alcohol, 15.81 g of pyridine, and 18.9 g of 2-ethoxyvinylphosphonic dichloride was 20 g (75%) of the ester, b.p. 107° (0.5 mm); d_4^{20} 1.0004; n_D^{24} 1.4453.

Found %: C 54.72; 54.31; H 9.20; 9.35
$C_{12}H_{25}O_4P$. Calculated %: C 54.54; H 9.46

TABLE 4

Formula of compound	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}
$n\text{-}C_6H_{13}-O-CH{=}CHPO\,(OCH_3)_2$	125 (2)	1.4530	1.0498
$n\text{-}C_6H_{13}-O-CH{=}CHPO\,(OC_2H_5)_2$	136 (2)	1.4495	1.0110
$n\text{-}C_6H_{13}-O-CH{=}CHPO\,(OC_3H_7\text{-n})_2$	138–139 (2)	1.4500	0.9891
$n\text{-}C_6H_{13}-O-CH{=}CHPO\,(OC_3H_7\text{-i})_2$	129 (2)	1.4402	0.9804
$n\text{-}C_6H_{13}-O-CH{=}CHPO\,(OC_4H_9\text{-n})_2$	156 (1)	1.4496	0.9723
$n\text{-}C_6H_{13}-O-CH{=}CHPO\,(OC_4H_9\text{-i})_2$	151 (1)	1.4475	0.9660
$n\text{-}C_6H_{13}-O-CH{=}CHPO\,(OC_3H_5)_2$	151 (1)	1.4650	1.0178
$n\text{-}C_6H_{13}-O-CH{=}CHPO\,(OC_6H_{13}\text{-n})_2$	190 (2)	1.4528	0.9515
$n\text{-}C_6H_{13}-O-CH{=}CHPO\,(OCH_2-CH_2-OCH_3)_2$	171 (2)	1.4560	1.0632
$n\text{-}C_6H_{13}-O-CH{=}CHPO\,(OCH_2-CH_2-OC_2H_5)_2$	188 (2)	1.4593	1.0348

Diallyl 2-Ethoxyvinylphosphonate $C_2H_5OCH{=}CHPO\,(OC_3H_5)_2$. The product obtained from 11.6 g of allyl alcohol, 15.8 g of pyridine, and 18.9 g of 2-ethoxyvinylphosphonic dichloride was 13 g (56%) of the ester, b.p. 112° (1 mm); d_4^{20} 1.0792; n_D^{20} 1.4698.

Found %: C 51.62; 51.38; H 7.28; 7.38
$C_{10}H_{17}O_4P$. Calculated %: C 51.72; H 7.32

Dihexyl 2-Ethoxyvinylphosphonate $C_2H_5OCH{=}CHPO(OC_6H_{13}\text{-n})_2$. 2-Ethoxyvinylphosphonic dichloride (9.45 g) was added to 10.21 g of hexyl alcohol and 7.9 g of pyridine. and 9 g of dihexyl 2-ethoxyvinylphosphonate was isolated. It had b.p. 157-158° (2 mm); d_4^{20} 0.9710; n_D^{20} 1.4511

Found %: C 60.40; 60.38; H 10.31; 10.35
$C_{16}H_{33}O_4P$. Calculated %: C 60.00; H 10.31

Bis(2-methoxyethyl) 2-Ethoxyvinylphosphonate $C_2H_5OCH{=}CHPO(OCH_2-CH_2-OCH_3)_2$. The product obtained from 15 g of 2-methoxyethanol, 15.8 g of pyridine, and 18.9 g of 2-ethoxyvinylphosphonic dichloride was 20 g (76%) of a substance of b.p. 155° (2 mm); d_4^{20} 1.1267; n_D^{20} 1.4568.

Found %: P 11.46; 11.45
$C_{10}H_{21}O_6P$. Calculated %: P 11.56

Bis(2-ethoxyethyl) 2-Ethoxyvinylphosphonate $C_2H_5OCH{=}CHPO(OCH_2-CH_2-OC_2H_5)_2$. The product obtained from 18 g of 2-ethoxyethanol, 15.8 g of pyridine, and 18.9 g of 2-ethoxyvinylphosphonic dichloride was 22 g (70%) of a substance of b.p. 158° (1 mm); d_4^{20} 1.0842; n_D^{20} 1.4545

Found %: P 10.47; 10.42
$C_{12}H_{25}O_6P$. Calculated %: P 10.47

Diesters of 2-Propoxyvinylphosphonic Acid

Dimethyl 2-Propoxyvinylphosphonate n-$C_3H_7OCH{=}CHPO(OCH_3)_2$. 2-Propoxyvinylphosphonic dichloride (10.15 g) was added to a mixture of 3.2 g of methanol, 7.9 g of pyridine, and 80 ml of benzene. The substance isolated (6.5 g) had b.p. 95° (1 mm); d_4^{20} 1.1095; n_D^{20} 1.4500.

Found %: P 15.98; 15.76

$C_7H_{15}O_4P$. Calculated %: P 15.97

Diethyl 2-Propoxyvinylphosphonate n-$C_3H_7{-}O{-}CH{=}CHPO(OC_2H_5)_2$. The product obtained from 4.6 g of ethanol, 7.9 g of pyridine, and 10.15 g of 2-propoxyvinylphosphonic dichloride was 7.5 g of a substance of b.p. 106° (1 mm) d_4^{20} 1.0523; n_D^{20} 1.4455.

Found %: P 13.92; 13.96

$C_9H_{19}O_4P$. Calculated %: P 13.96

Dipropyl 2-Propoxyvinylphosphonate n-$C_3H_7OCH{=}CHPO(OC_3H_7\text{-}n)$. 2-Propoxyvinylphosphonic dichloride (10.15 g) was added to 6 g of propyl alcohol and 8 g of pyridine, and 7.3 g (60%) of dipropyl 2-propoxyvinylphosphonate was isolated. It had b.p. 128° (2 mm); d_4^{20} 1.0201; n_D^{20} 1.4471.

Found %: P 12.36; 12.29

$C_{11}H_{23}O_4P$. Calculated %: P 12.40

Diisopropyl 2-Propoxyvinylphosphonate n-$C_3H_7OCH{=}CHPO(OC_3H_7\text{-}i)_2$. 2-Propoxyvinylphosphonic dichloride (10.15 g) was added to 6 g of isopropyl alcohol and 8 g of pyridine, and the product was 7.2 g of a substance of b.p. 110° (2 mm); d_4^{20} 1.0042; n_D^{20} 1.4402.

Found %: P 12.33; 12.29

$C_{11}H_{23}O_4P$. Calculated %: P 12.40

Dibutyl 2-Propoxyvinylphosphonate n-$C_3H_7OCH{=}CHPO(OC_4H_9\text{-}n)_2$. The product obtained from 7.4 g of butyl alcohol, 8 g of pyridine, and 10.15 g of 2-propoxyvinylphosphonic dichloride was 8.5 g (64%) of a substance of b.p. 139° (2 mm); d_4^{20} 0.9969 . n_D^{20} 1.4485.

Found %: P 10.99; 11.17

$C_{13}H_{27}O_4P$. Calculated %: P 11.15

Diisobutyl 2-Propoxyvinylphosphonate n-$C_3H_7OCH{=}CHPO(OC_4H_9\text{-}i)_2$. Isobutyl alcohol was substituted for butyl alcohol in the above synthesis, the amounts taken and the reaction conditions being exactly the same. The product (9.7 g) had b.p. 121° (2 mm); d_4^{20} 0.9906; n_D^{20} 1.4449.

Found %: C 55.77; 55.72; H 9.82; 9.72; P 11.23; 11.22;

$C_{13}H_{27}O_4P$. Calculated %: C 56.11; H 9.71; P 11.15

Diallyl 2-Propoxyvinylphosphonate n-$C_3H_7OCH{=}CHPO(OC_3H_5)_2$. The product obtained from 5.8 g of allyl alcohol, 8 g of pyridine, and 10.15 g of 2-propoxyvinylphosphonic dichloride was 7 g of diallyl 2-propoxyvinylphosphonate, b.p. 123° (1 mm); d_4^{20} 1.0557; n_D^{20} 1.4675.

Found %: C 55.63; 53.53; H 7.79; 7.88

$C_{11}H_{19}O_4P$. Calculated %: C 53.65; H 7.72

Dihexyl 2-Propoxyvinylphosphonate n-$C_3H_7OCH{=}CHPO(OC_6H_{13}\text{-}n)_2$. 2-Propoxyvinylphosphonic dichloride (10.15 g) was added to 10.21 g of hexyl alcohol and 7.8 g of pyridine. The product (9.5 g) had b.p. 157° (1 mm); d_4^{20} 0.9664; n_D^{20} 1.4509.

Found %: P 8.96; 9.13

$C_{17}H_{35}O_4P$. Calculated %: P 9.25

Bis(2-methoxyethyl) 2-Propoxyvinylphosphonate n-$C_3H_7OCH{=}CHPO(OCH_2{-}CH_2OCH_3)_2$. 2-Propoxyvinylphosphonic dichloride (10.15 g) was added to 7.6 g of 2-methoxyethanol and 7.9 g of pyridine. The product (9 g) had b.p. 158° (1 mm); d_4^{20} 1.1089; n_D^{20} 1.4565.

Found %: C 47.12; 46.93; H 8.35; 8.26

$C_{11}H_{23}O_6P$. Calculated %: C 46.80; H 8.15

Bis(2-ethoxyethyl) 2-Propoxyvinylphosphonate n-$C_3H_7OCH{=}CHPO(OCH_2{-}CH_2OC_2H_5)_2$. The product obtained from 9 g of 2-ethoxyethanol, 7.9 g of pyridine, and 10.15 g of 2-propoxyvinylphosphonic dichloride was 10 g of a substance of b.p. 156° (1 mm); d_4^{20} 1.0694; n_D^{20} 1.4580.

Found %: C 50.33; 50.40; H 8.78; 8.82

$C_{13}H_{27}O_5P$. Calculated %: C 50.32; H 8.70

Diesters of 2-Butoxyvinylphosphonic Acid

Dimethyl 2-Butoxyvinylphosphonate n-$C_4H_9OCH=CHPO(OCH_3)_2$. 2-Butoxyvinylphosphonic dichloride (21.7 g) was added to 6.4 g of methanol and 15.8 g of pyridine. The product was 11 g (51%) of a substance of b.p. 111° (2 mm); d_4^{20} 1.0867; n_D^{20} 1.4515.

Found %: C 46.32; 46.35; H 8.06; 8.00

$C_8H_{17}O_4P$. Calculated %: C 46.15; H 8.17

Diethyl 2-Butoxyvinylphosphonate n-$C_4H_9OCH=CHPO(OC_2H_5)_2$. 2-Butoxyvinylphosphonic dichloride (10.85 g) was added to 4.6 g of absolute ethanol and 7.9 g of pyridine. An ester was isolated having b.p. 116.5° (2 mm); d_4^{20} 1.0360; n_D^{20} 1.4460.

Found %: C 50.53; 50.66; H 8.65; 8.80

$C_{10}H_{21}O_4P$. Calculated %: C 50;84; H 8.89

Dipropyl 2-Butoxyvinylphosphonate n-$C_4H_9OCH=CHPO(OC_3H_7\text{-}n)_2$. The product obtained from 10.85 g of 2-butoxyvinylphosphonic dichloride, 6 g of propyl alcohol, and 7.9 g of pyridine was 9 g (68%) of a substance of b.p. 123° (2 mm); d_4^{20} 1.0060; n_D^{23} 1.4478.

Found %: C 54.40; 54.48; H 9.34; 9.49

$C_{12}H_{25}O_4P$. Calculated %: C 54.54; H 9.46

Diisopropyl 2-Butoxyvinylphosphonate n-$C_4H_9OCH=CHPO(OC_3H_7\text{-}i)_2$. The product obtained from 6 g of isopropyl alcohol, 7.9 g of pyridine, and 10.85 g of 2-butoxyvinylphosphonic dichloride was 5 g of a substance of b.p. 105° (2 mm); d_4^{20} 0.9916; n_D^{20} 1.4401.

Found %: C 54.19; 54.23; H 9.36; 9.46

$C_{12}H_{25}O_4P$. Calculated %: C 54.54; H 9.46

Dibutyl 2-Butoxyvinylphosphonate n-$C_4H_9OCH=CHPO(OC_4H_9\text{-}n)_2$. The product obtained from 7.4 g of butyl alcohol, 7.9 g of pyridine, and 10.85 g of 2-butoxyvinylphosphonic dichloride was 9 g (67%) of an ester of b.p. 144° (2 mm); d_4^{20} 0.9879, n_D^{20} 1.4491.

Found %: C 57.87; 57.80; H 9.99; 9.96

$C_{14}H_{25}O_4P$. Calculated %: C 57.53; H 9.93

Diisobutyl 2-Butoxyvinylphosphonate n-$C_4H_9OCH=CHPO(OC_4H_9\text{-}i)_2$. 2-Butoxyvinylphosphonic dichloride (10.85 g) was added to 7.4 g of isobutyl alcohol and 7.9 g of pyridine. The product was 8.5 g (63%) of a substance of b.p. 131.5° (2 mm); d_4^{20} 0.9810; n_D^{20} 1.4460.

Found %: C 57.01; 57.06; H 10.16; 10.15

$C_{14}H_{29}O_4P$. Calculated %: C 57.53; H 9.93

Diallyl 2-Butoxyvinylphosphonate n-$C_4H_9OCH=CHPO(OC_3H_5)_2$. The product obtained from 10.85 g of 2-butoxyvinylphosphonic dichloride, 5.8 g of allyl alcohol, and 7.9 g of pyridine was 7 g (50%) of an ester of b.p. 139.5° (2 mm) d_4^{20} 1.0442; n_D^{25} 1.4651.

Found %: C 54.88; 55.09; H 8.05; 7.88

$C_{12}H_{21}O_4P$. Calculated %: C 55.38; H 8.07

Dihexyl 2-Butoxyvinylphosphonate n-$C_4H_9OCH=CHPO(OC_6H_{13}\text{-}n)_2$. The product obtained from 10.21 g of hexyl alcohol, 7.9 g of pyridine, and 10.85 g of 2-butoxyvinylphosphonic dichloride was 10 g (57%) of a substance of b.p. 164–165° (2 mm); d_4^{20} 0.9635; n_D^{20} 1.4518.

Found %: C 62.13; 61.99; H 10.58; 10.89

$C_{18}H_{37}O_4P$. Calculated %: C 62.06; H 10.63

Bis(2-methoxyethyl) 2-Butoxyvinylphosphonate n-$C_4H_9OCH=CHPO(OCH_2-CH_2OCH_3)_2$. 2-Butoxyvinylphosphonic dichloride (21.05 g) was added to 14.57 g of 2-methoxyethanol and 15.28 g of pyridine. The product was 16 g (55%) of a substance of b.p. 161° (2 mm); d_4^{20} 1.0873; n_D^{20} 1.4558

Found %: P 10.32; 10.55

$C_{12}H_{25}O_4P$. Calculated %: P 10.47

Bis(2-ethoxyethyl) 2-Butoxyvinylphosphonate $n\text{-}C_4H_9OCH{=}CHPO(OCH_2{-}CH_2OC_2H_5)_2$. The product obtained from 9 g of 2-ethoxyethanol, 7.9 g of pyridine, and 10.85 g of 2-butoxyvinylphosphonic dichloride was 8 g (50%) of an ester of b.p. 164° (2 mm); d_4^{20} 1.0584; n_D^{20} 1.4532.

Found %: P 9.28; 9.43

$C_{14}H_{29}O_6P$. Calculated %: P 9.56

Diesters of 2-(Hexyloxy)vinylphosphonic Acid.

Dimethyl 2-(Hexyloxy)vinylphosphonate $n\text{-}C_6H_{13}OCH{=}CHPO(OCH_3)_2$. The product obtained from 3.2 g of methanol, 7.9 g of pyridine and 12.25 g of 2-(hexyloxy)vinylphosphonic dichloride was 6 g of an ester of b.p. 125° (22 mm); d_4^{20} 1.0498; n_D^{20} 1.4530.

Found %: C 50.68; 50.80; H 8.95; 8.82

$C_{10}H_{21}O_4P$. Calculated % C 50.84; H 8.89

Diethyl 2-(Hexyloxy)vinylphosphonate $n\text{-}C_6H_{13}OCH{=}CHPO(OC_2H_5)_2$. The product obtained from 4.6 g of ethanol, 7.9 g of pyridine, and 12.28 g of 2-(hexyloxy)vinylphosphonic dichloride was 8 g of a substance of b.p. 136° (2 mm); d_4^{20} 1.0110; n_D^{20} 1.4495.

Found %: P 11.68; 11.71

$C_{12}H_{25}O_4P$. Calculated %: P 11.75

Dipropyl 2-(Hexyloxy)vinylphosphonate $n\text{-}C_6H_{13}OCH{=}CHPO(OC_3H_7\text{-}n)_2$. 2-(Hexyloxy)vinylphosphonic dichloride (12.25 g) was added to 6 g of propyl alcohol and 7.9 g of pyridine. The product was 11 g of an ester of b.p. 138–139° (1 mm); d_4^{20} 0.9891; n_D^{20} 1.4500.

Found %: P 10.34; 10.57

$C_{14}H_{29}O_4P$. Calculated %: P 10.61

Diisopropyl 2-(Hexyloxy)vinylphosphonate $n\text{-}C_6H_{13}OCH{=}CHPO(OC_3H_7\text{-}i)_2$. The product obtained from 6 g of isopropyl alcohol, 7.9 g of pyridine, and 12.25 g of 2-(hexyloxy)vinylphosphonic dichloride was 5 g of a substance of b.p. 129° (1 mm); d_4^{20} 0.9804; n_D^{20} 1.4402.

Found %: P 10.86; 10.87

$C_{14}H_{29}O_4P$. Calculated %: P 10.61

Dibutyl 2-(Hexyloxy)vinylphosphonate $n\text{-}C_6H_{13}OCH{=}CHPO(OC_4H_9\text{-}n)_2$. The product obtained from 7.4 g of butyl alcohol, 7.9 g of pyridine and 12.25 g of 2-(hexyloxy)vinylphosphonic dichloride was 12 g of an ester of b.p. 156° (1 mm); d_4^{20} 0.9723; n_D^{20} 1.4496.

Found %: C 60.07; 60.09; H 10.63; 10.62

$C_{16}H_{33}O_4P$. Calculated %: C 60.00; H 10.31

Diisobutyl 2-(Hexyloxy)vinylphosphonate $n\text{-}C_6H_{13}OCH{=}CHPO(OC_4H_9\text{-}i)_2$. 2-(Hexyloxy)vinylphosphonic dichloride (12.25 g) was added to 7.4 g of isobutyl alcohol and 7.9 g of pyridine. The product was an ester (9 g) of b.p. 151° (1 mm); d_4^{20} 0.9660; n_D^{20} 1.4475.

Found %: C 60.37; 60.28; H 10.54; 10.55

$C_{16}H_{33}O_4P$. Calculated %: C 60.00; H 10.31

Diallyl 2-(Hexyloxy)vinylphosphonate $n\text{-}C_6H_{13}OCH{=}CHPO(OC_3H_5)_2$. The product obtained from 5.8g of allyl alcohol, 7.9 g of pyridine, and 12.25 g of 2-(hexyloxy)vinylphosphonic dichloride was 8 g of a substance, b.p. 151° (1 mm). d_4^{20} 1.0178; n_D^{20} 1.4650.

Found %: C 58.07; 58.16; H 8.60; 8.78

$C_{14}H_{25}O_4P$. Calculated %: C 58.33; H 8.68

Dihexyl 2-(Hexyloxy)vinylphosphonate $n\text{-}C_6H_{13}OCH{=}CHPO(OC_6H_{13}\text{-}n)_2$. The product obtained from 10.21 g of hexyl alcohol, 7.9 g of pyridine, and 12.21 g of 2-(hexyloxy)vinylphosphonic dichloride was an ester (11 g) of b.p. 190° (2 mm); d_4^{20} 0.9515; n_D^{20} 1.4528.

Found %: C 64.00; 63.79; H 10.93; 11.16

$C_{20}H_{41}O_4P$. Calculated %: C 63.82; H 10.90

Bis(2-methoxyethyl) 2-(Hexyloxy)vinylphosphonate $n\text{-}C_6H_{13}OCH{=}CHPO(OCH_2{-}CH_2{-}OCH_3)_2$. The product obtained from 7.6 g of 2-methoxyethanol and 12.25 g of 2-(hexyloxy)vinylphosphonic dichloride in presence of 7.9 g of pyridine was 7.4 g of a substance of b.p. 171° (1 mm); d_4^{20} 1.0632; n_D^{20} 1.4560.

Found %: P 9.50; 9.42

$C_{14}H_{29}O_6P$. Calculated %: P 9.56

Bis (2-ethoxyethyl) 2-(Hexyloxy)vinylphosphonate $n\text{-}C_6H_{13}OCH{=}CHPO(OCH_2{-}CH_2OC_2H_5)_2$. 2-(Hexyloxy)vinylphosphonic dichloride (12.25 g) was added to 9 g of 2-ethoxyethanol and 7.9 g of pyridine. The product was an ester (8 g) of b.p. 188° (1 mm); d_4^{20} 1.0348; n_D^{20} 1.4593.

Found %: C 54.39; 54.31; H 9.56; 9.58

$C_{16}H_{33}O_6P$. Calculated %: C 54.54; H 9.37

SUMMARY

1. Diesters of 2-ethoxy-, 2-propoxy-, 2-butoxy-, and 2-hexyloxy-vinylphosphonic acids have been synthesized by the action of alcohols in presence of pyridine on the corresponding 2-alkoxyvinylphosphonic dichlorides.

2. The dimethyl, diethyl, dipropyl, diisopropyl, dibutyl, diisobutyl, diallyl, dihexyl, bis(2-methoxyethyl), and bis(2-ethoxyethyl) esters of 2-ethoxy-, 2-propoxy-, 2-butoxy-, and 2-hexyloxy-vinylphosphonic acids have been prepared.

LITERATURE CITED

[1] K. N. Anisimov and A. N. Nesmeyanov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 4, 610.*

[2] A. E. Arbuzov and V. M. Zoroastrova, Selected Works, 509, 1952.

[3] A. E. Arbuzov and A. I. Razumov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1951, No. 6, 714.

[4] L. N. Parfentyev, Sci. Mem. Kazan State Univ., Book 1, 75 (1925).

[5] A. N. Pudovik and B. A. Arbuzov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1949, No. 5, 522.

[6] A. N. Pudovik, J. Gen. Chem., 20, 92 (1950).**

[7] A. N. Pudovik and B. A. Arbuzov, Proc. Acad. Sci. USSR, 73, No. 2, 327 (1950); J. Gen. Chem., 21, 2,382 (1951).***

[8] A. N. Pudovik, Proc. Acad. Sci. USSR, 73, No. 3, 499 (1950).

[9] A. N. Pudovik and Yu. P. Kitaev, J. Gen. Chem., 22, 467 (1952)****

[10] A. E. Arbuzov and V. M. Zoroastrova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1950, No. 4, 357.

[11] M. I. Kabachnik, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1947, No. 2, 233.

[12] A. N. Pudovik and N. P. Denisova, Coll. Papers on General Chem., Acad. Sci. USSR Press, 1, 388, 1953.

[13] T. Milobendzski, A. Sachnowski, Chem. Polsk. 15, 34 (1917).

Received June 11, 1954

Institute of Heteroorganic Compounds of the
USSR Academy of Sciences

---

* See Consultants Bureau Translation, p. 521.

** See Consultants Bureau Translation, p. 83.

*** See Consultants Bureau Translation, p. 423.

**** See Consultants Bureau Translation, p. 531

THE PRODUCTS OF THE ACTION OF SODIUM DIETHYL PHOSPHOROTHIONATE ON ALKYL PHOSPHORODICHLORIDITES

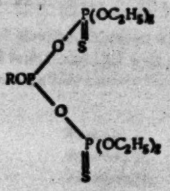
B. A. Arbuzov and P. I. Alimov

Derivatives of pyrophosphoric and triphosphoric acids and of their sulfur analogs are at present attracting much attention owing to the fact that pyrophosphoric and triphosphoric groupings have been found in some physiologically active compounds, such as vitamins, nucleotides, and coenzymes, and also because many derivatives of pyrophosphoric acid and its sulfur analogs have been found to be powerful insecticides.

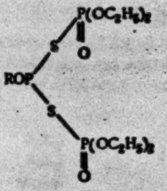
In this paper we describe the preparation and some of the properties of esters of an acid that can be regarded as an anhydride formed from two molecules of phosphorothionic acid and one molecule of phosphorous acid. Esters of general formula $ROP[OPS(OC_2H_5)_2]_2$ have been prepared by us for the first time by the action of sodium diethyl phosphorothionate on alkyl phosphorodichloridites, which proceeds according to the equation

$$ROPCl_2 + 2NaOPS(OC_2H_5)_2 = ROP[OPS(OC_2H_5)_2]_2 + 2NaCl.$$

Sodium diethyl phosphorothionate was prepared by the addition of sulfur to sodium diethyl phosphite. The structure of the reaction products can be represented by formulas in which phosphorus atoms are united through oxygen or sulfur



(I)



(II)

On the basis of the method of preparation from sodium diethyl phosphorothionate, formula (I) appears to be more probable but as it is possible that sodium may move from oxygen to sulfur, the question of which of the formulas (I) and (II) represents the structure of these compounds must remain open.

In the preparation of the alkyl phosphite – diethyl phosphorothionate anhydrides the alkyl phosphorodichloridites used as starting materials were methyl, ethyl, propyl, isopropyl, and isobutyl phosphorodichloridites. When treated with sodium diethyl phosphorothionate, these acid chlorides yielded the compounds listed with their constants in the table.

TABLE 1

No.	R	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}	Yield (%)
1	CH_3	164-165 (2)	1.4837	1.2287	22.8
2	C_2H_5	160-161 (1)	1.4815	1.2069	25.4
3	$i-C_3H_7$	170-171 (3.5)	1.4800	1.1863	8.8
4	$n-C_3H_7$	168-169 (2.5)	1.4780	1.1901	32.4
5	$i-C_4H_9$	166-167 (1.5)	1.4802	1.1747	40.2

All of the substances given in the table are colorless mobile liquids having odors characteristic of sulfur compounds. They are soluble in water and in organic solvents. The yields of the pure substances were 20-40%. One of the causes of the low yields of the products is their instability at the high temperatures employed in the distillation (bath temperature 200-215°). These anhydrides of alkyl hydrogen phosphite with diethyl hydrogen phosphorothionate react with cuprous halides stoichiometrically with evolution of heat (A. E. Arbuzov's reaction for tervalent phosphorus), but we have not succeeded in isolating individual products, noncrystallizing sirups being obtained.

In spite of the fact that one of the phosphorus atoms of the compounds described is tervalent, they do not unite with sulfur under the conditions that result in the ready addition of sulfur to other organophosphorus compounds, e.g. trialkyl phosphites.

EXPERIMENTAL

1. The Ethyl Phosphite – Diethyl Phosphorothionate Anhydride $C_2H_5OP[OPS(OC_2H_5)_2]_2$.

Sodium diethyl phosphorothionate was prepared from 30.2 g of diethyl hydrogen phosphite, 5 g of sodium, and 7 g of sulfur in 100 ml of gasoline (b.p. 70-125°), and the mixture was stirred at room temperature while ethyl phosphorodichloridite was added slowly. The flask and contents were heated in a water bath and then cooled. Sodium chloride was centrifuged off, and gasoline was distilled off under reduced pressure. The residue (30 g, i.e. 66.3%) was fractionated, and the following fractions were obtained at a residual pressure of 1 mm:

Fraction I,	B.p. 85-150°;	4 g
Fraction II,	B.p. 150-160°;	6 g
Fraction III,	B.p. 160.5-161°;	12 g

Redistillation of Fractions II and III yielded 11.5 g (25.4%) of a substance of b.p. 160-161° (1 mm); n_D^{20} 1.4815; d_4^{20} 1.2069.

Found %: P 22.31; 22.32; S 15.32; 15.37

$C_{10}H_{25}P_3S_2O_7$. Calculated %: P 22.46; S 15.46

It was a colorless mobile liquid having a sulfurous odor. It was soluble in water and in organic solvents.

2. The Methyl Phosphite – Diethyl Phosphorothionate Anhydride $CH_3OP[OPS(OC_2H_5)_2]_2$.

Sodium diethyl phosphorothionate was prepared in gasoline from 27.2 g of diethyl hydrogen phosphite, 4.5 g of sodium, and 6.3 g of sulfur, and 13.1 g of methyl phosphorodichloridite was added. The yield of crude product was 29.8 g (75.6%) (a pale-yellow mobile liquid). The first distillation from an Arbuzov flask at 2 mm gave the following fractions:

Fraction I,	B.p.	75-154°;	3.2 g
Fraction II,	B.p.	154-162°;	3.3 g
Fraction III,	B.p.	162-165°;	10.5 g
Residue			12 g

Refractionation of Fractions II and III yielded 9 g (28.8%) of a substance of b.p. 164-165°; (2 mm); n_D^{20} 1.4837; d_4^{20} 1.2287

Found %: P 23.03; 23.03; S 15.75; 15.69

$C_9H_{23}P_3S_2O_7$. Calculated %: P 23.25 S 16.00

3. The Isopropyl Phosphite – Diethyl Phosphorothionate Anhydride $i\text{-}C_3H_7OP[OPS(OC_2H_5)_2]_2$

The reactants were 17.5 g of isopropyl phosphorodichloridite and sodium diethyl phosphorothionate prepared from 30 g of diethyl hydrogen phosphite, 5 g of sodium, and 6.9 g of sulfur. The reaction was carried out in gasoline (b.p. 75-125°). The yield of crude product was 35 g (88.3%) (a mobile yellowish-green liquid). The first distillation was carried out at 4 mm in a Claisen flask having a low delivery tube. The fractions obtained were:

Fraction I	B.p.	to 145°;	4 g
Fraction II	B.p.	145-171°;	9 g
Fraction III	B.p.	171-176°;	3.5 g
Residue			17 g

Refractionation of Fractions II and III was carried out from an Arbuzov flask. The product was 3.5 g (8.8%) of a substance of b.p. 170-171° (3.5 mm); n_D^{20} 1.4800; d_4^{20} 1.1863.

Found %: P 21.61; 21.8; S 14.9; 15.08

$C_{11}H_{27}P_3S_2O_7$. Calculated %: P 21.72; S 14.95

4. The Propyl Phosphite – Diethyl Phosphorothionate Anhydride $n\text{-}C_3H_7OP[OPS(OC_2H_5)_2]_2$

Propyl phosphorodichloridite (19 g) was added to sodium diethyl phosphorothionate prepared from 32.6 g of diethyl hydrogen phosphite, 5.4 g of sodium, and 7.5 g of sulfur in 100 ml of gasoline (b.p. 70-125°). The yield of crude product was 41.2 g (81.5%). Two distillations yielded a fraction of b.p. 168-169° (2.5 mm); n_D^{20} 1.4780; d_4^{20} 1.1901. The yield was 16.4 g (32.4%).

Found %: P 21.49; 21.61

$C_{11}H_{27}P_3S_2O_7$. Calculated %: P 21.72

This substance was a mobile liquid, readily soluble in water and in organic solvents.

5. The Isobutyl Phosphite – Diethyl Phosphorothionate Anhydride i-$C_4H_9OP[OPS(OC_2H_5)_2]_2$.

This was prepared by the same procedure by the action of isobutyl phosphorodichloridite (17.2 g) on sodium diethyl phosphorothionate prepared from 27.2 g of diethyl hydrogen phosphite, 4.5 g of sodium, and 6.3 g of sulfur. Two distillations of the crude product from an Arbuzov flask yielded a fraction of b.p. 166-167° (1.5 mm); n_D^{23} 1.4802; d_4^{20} 1.1747. The yield was 17.5 g (40.2%).

Found %: P 21.09; 20.75; S 14.66; 14.62

$C_{12}H_{29}P_3S_2O_7$. Calculated %: P 21.04; S 14.48

6. Action of Cuprous Bromide on the Ethyl Phosphite – Bis[Diethyl Phosphorothionate] Anhydride.

The ester (1.2 g) was placed in a test tube, and an equimolecular amount (0.41 g) of cuprous bromide was added. Part of the salt dissolved at room temperature, and the temperature of the mixture rose from 24° to 35°. The test tube was heated in an oil bath at 140-150°. The whole of the salt rapidly dissolved, and a clear solution was formed. The resulting viscous liquid did not crystallize even after standing for a long time.

SUMMARY

By the action of alkyl phosphorodichloridites $ROPCl_2$ (R = methyl, ethyl, isopropyl, propyl, and isobutyl) on sodium diethyl phosphorothionate $(C_2H_5O)_2PSONa$, anhydrides of alkyl dihydrogen phosphite with two molecules of diethyl hydrogen phosphorothionate of general formula $ROP[OPS(OC_2H_5)_2]_2$ have been prepared for the first time, and some of their properties have been studied.

Received January 16, 1954.

A. E. Arbuzov Chemical Institute of the Kazan Affiliated
Institute of the USSR Academy of Sciences

BLANK
PAGE

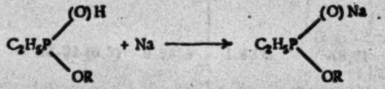
ESTERS OF ETHYLPHOSPHONOUS ACID, AND SOME OF THEIR REACTIONS

COMMUNICATION 5. SYNTHESIS OF ESTERS OF DIALKYLPHOSPHINIC ACIDS

B. A. Arbuzov and N. I. Rizpolozhensky

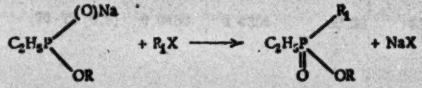
Continuing our study of the monoesters of the ethylphosphonous acid that we have synthesized [1], we have prepared some esters of dialkylphosphinic acids. We have already [2] prepared some dialkylphosphinic esters, including some containing unlike radicals on the phosphorus, by application of the Arbuzov rearrangement [3] in a study of the chemical properties of the diesters of ethylphosphonous acid, but it should be noted that the yields of the mixed-radical esters were rather low (25-30%).

Razumov and Mukhacheva [4] prepared dialkylphosphinic esters by the action of alcohols on dialkylphosphinic chlorides. Michaelis and Becker [5] showed that sodium dialkyl phosphites react with certain halogen compounds with formation of esters of alkylphosphonic acids, and we considered that it would be of interest to examine the possibility of applying this reaction for the synthesis of dialkylphosphinic esters, particularly those having unlike radicals on the phosphorus. It was found that the acid esters of ethylphosphonous acid, like those of phosphorous acid, react with sodium with formation of the sodium derivatives according to the equation.



These sodium derivatives are soluble in ether, gasoline, and benzene.

Alkyl halides react with sodium alkyl ethylphosphonites with formation of dialkylphosphinic esters according to the equation:



Using this reaction we have prepared some dialkylphosphinic esters having unlike radicals on the phosphorus, and the yields have been satisfactory (50-60% on the average). The principal physicochemical constants of these esters are given in the table.

EXPERIMENTAL

Synthesis of Dialkylphosphinic Esters

1. Ethyl Ethylhexylphosphinate. Ether (50-60 ml) and sodium (0.8 g, an excess) were placed in a three-necked flask fitted with a mercury-sealed mechanical stirrer, a reflux condenser, and a dropping funnel. Ethyl hydrogen ethylphosphonite (3.7 g) was added from the funnel, and the flask was heated in a water bath for 1.5-2 hours. The excess of sodium was then removed, and the ethereal solution of sodium ethyl ethylphosphonite was then boiled while addition was made of 6.4 g of hexyl iodine. The flask was heated for a further 1-1.5 hours in a water bath.

The precipitate of sodium iodide was removed by centrifugation. The residue remaining after removal of ether was vacuum-fractionated from an Arbuzov flask, and the ethyl ethylhexylphosphinate obtained had the following constants: b.p. 93° (0.5 mm); d_4^{20} 0.9302; n_D^{20} 1.4413.

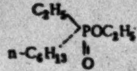
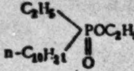
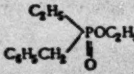
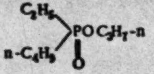
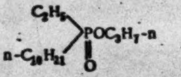
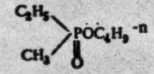
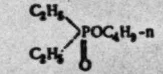
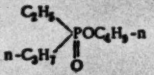
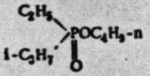
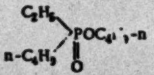
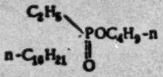
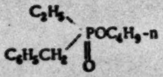
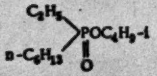
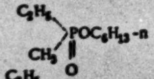
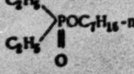
Found: MR 58.38

$C_{10}H_{23}PO_2$. Calculated: MR 58.33

Found %: P 14.85; 14.92

$C_{10}H_{23}PO_2$. Calculated %: P 15.03

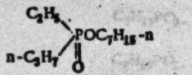
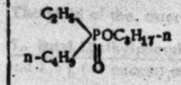
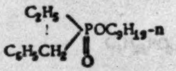
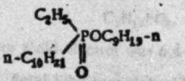
TABLE*

No.	Formula	B.p. in °C (p in mm Hg)	d_4^{20}	n_D^{20}	MR		Yield (%)
					found	calculated	
1	 $(C_2H_5)(n\text{-}C_6H_{13})P(=O)OC_2H_5$	93 (0.5)	0.9302	1.4413	58.38	58.33	48
2	 $(C_2H_5)(n\text{-}C_{10}H_{21})P(=O)OC_2H_5$	130-131 (1)	0.9160	1.4480	76.68	76.82	50
3	 $(C_2H_5)(C_6H_5CH_2)P(=O)OC_2H_5$	115-115.5 (1)	1.0793	1.5122	59.02	59.14	61
4	 $(C_2H_5)(n\text{-}C_4H_9)P(=O)OC_3H_7\text{-}n$	119-120 (10)	0.9483	1.4395	53.31	53.50	54
5	 $(C_2H_5)(n\text{-}C_{10}H_{21})P(=O)OC_3H_7\text{-}n$	140-141 (1)	0.9129	1.4478	81.03	81.20	45
6	 $(C_2H_5)(CH_3)P(=O)OC_4H_9\text{-}n$	73-74 (1.5)	0.9689	1.4350	44.45	44.26	54
7	 $(C_2H_5)(C_2H_5)P(=O)OC_4H_9\text{-}n$	80-81 (0.5)	0.9588	1.4371	48.71	48.88	63
8	 $(C_2H_5)(n\text{-}C_3H_7)P(=O)OC_4H_9\text{-}n$	83-84 (0.5)	0.9461	1.4381	53.36	53.50	66
9	 $(C_2H_5)(i\text{-}C_3H_7)P(=O)OC_4H_9\text{-}n$	70-72 (0.5)	0.9452	1.4365	53.23	53.50	26
10	 $(C_2H_5)(n\text{-}C_4H_9)P(=O)OC_4H_9\text{-}n$	89-90 (0.5)	0.9372	1.4400	57.98	58.01	71
11	 $(C_2H_5)(n\text{-}C_{10}H_{21})P(=O)OC_4H_9\text{-}n$	148-150 (1.5)	0.9083	1.4489	85.75	85.82	54
12	 $(C_2H_5)(C_6H_5CH_2)P(=O)OC_4H_9\text{-}n$	124-125 (0.5)	1.0397	1.5050	69.14	69.37	71
13	 $(C_2H_5)(n\text{-}C_6H_{13})P(=O)OC_4H_9\text{-}i$	106-107 (0.5)	0.9235	1.4413	67.05	67.35	51
14	 $(C_2H_5)(CH_3)P(=O)OC_6H_{13}\text{-}n$	132-133 (12)	0.9483	1.4391	53.22	53.51	51
15	 $(C_2H_5)(C_2H_5)P(=O)OC_7H_{15}\text{-}n$	106-107 (0.5)	0.9332	1.4433	62.63	62.74	53

---

[*] In accordance with Kosolapoff's results [6], the atomic refraction of phosphorus is taken as 4.79.

TABLE 1 (Continued

No.	Formula	B.p. in °C (p in mm Hg)	d_4^{20}	n_D^{20}	MR		Yield (%)
					found	calculated	
16	 $(C_2H_5)(n\text{-}C_3H_7)P(O)OC_7H_{15}\text{-}n$	111-113 (0.5)	0.9262	1.4438	67.18	67.36	60
17	 $(C_2H_5)(n\text{-}C_4H_9)P(O)OC_8H_{17}\text{-}n$	133-134 (1)	0.9159	1.4467	76.49	76.59	40
18	 $(C_2H_5)(C_6H_5CH_2)P(O)OC_9H_{19}\text{-}n$	164-166 (0.5)	0.9314	1.4948	92.20	92.30	52
19	 $(C_2H_5)(n\text{-}C_{10}H_{21})P(O)OC_9H_{19}\text{-}n$	181-182 (0.5)	0.8947	1.4521	108.74	108.91	61

The yield of the ester was 3.1 g (48%).

In all of the succeeding experiments on the synthesis of dialkylphosphinic esters, the same procedure was employed.

2. Ethyl Decylethylphosphinate. The reactants were 2.8 g of ethyl hydrogen ethylphosphonite, 4.9 g of decyl bromide, and 0.8 g (an excess) of sodium. The resulting ester had the following constants: b.p. 130-131° (1 mm); d_4^{20} 0.9160; n_D^{20} 1.4480

Found : MR 76.68

$C_{14}H_{31}PO_2$. Calculated : MR 76.88

Found % : P 12.05; 11.86

$C_{14}H_{31}PO_2$. Calculated % : P 11.81

The yield of the ester was 3.1 g (50%).

3. Ethyl Benzylethylphosphinate. The reactants were 3 g of ethyl hydrogen ethylphosphonite, 4.2 g of benzyl bromide, and 1.2 g (an excess) of sodium. The principal constants of the ester were: b.p. 115-115.5° (1 mm); d_4^{20} 1.0793; n_D^{20} 1.5122.

Found : MR 59.02

$C_{11}H_{17}PO_2$. Calculated : MR 59.14

Found % P 14.48; 14.52

$C_{11}H_{17}PO_2$. Calculated % P 14.61

The yield of the ester was 3.2 g (61%).

4. Propyl Butylethylphosphinate. The reactants were 4.2 g of propyl hydrogen ethylphosphonite, 5.7 g of butyl iodide, and 0.9 g (an excess) of sodium. The constants of propyl butylethylphosphinate were: b.p. 119-120° (10 mm); d_4^{20} 0.9483; n_D^{20} 1.4395.

Found · MR 53.31

$C_9H_{21}PO_2$. Calculated ! MR 53.50

Found %: P 15.92; 15.98

$C_9H_{21}PO_2$. Calculated %: P 16.12

The yield of the ester was 3.22 g (54%).

5. Propyl Decylethylphosphinate. The reactants were 3.5 g of propyl hydrogen ethylphosphonite 5.7 g of decyl bromide and 1.2 g (an excess) of sodium. The ester obtained had the following constants: b.p. 140-141.5° (1 mm); d_4^{20} 0.9129; n_D^{20} 1.4478.

Found : MR 81.03

$C_{15}H_{33}PO_2$. Calculated : MR 81.20

Found % : P 11.31; 11.23

$C_{15}H_{33}PO_2$. Calculated % : P 11.47

The yield of the ester was 3.2 g (45%).

6. Butyl Ethylmethylphosphinate. The reactants were 6 g of butyl hydrogen ethylphosphonite, 5.7 g of methyl iodide, and 1.7 g (an excess) of sodium. The ester obtained had the following constants: b.p. 73-74° (1.5 mm); d_4^{20} 0.9689; n_D^{20} 1.4350.

Found MR 44.45
$C_7H_{17}PO_2$. Calculated MR 44.26
Found %: P 19.21; 19.26
$C_7H_{17}PO_2$. Calculated %: P 18.76

The yield of the ester was 3.6 g (54%).

7. Butyl Diethylphosphinate. The reactants were 7 g of butyl hydrogen ethylphosphonite, 5.1 g of ethyl bromide and 1.5 g (an excess) of sodium. The ester obtained had b.p. 80-81° (0.5 mm); d_4^{20} 0.9588; n_D^{20} 1.4371.

Found: MR 48.71
$C_8H_{19}PO_2$. Calculated: MR 48.88
Found %: P 17.48; 17.63
$C_8H_{19}PO_2$. Calculated %: P 17.39

The yield of ester was 5.4 g (63%).

8. Butyl Ethylpropylphosphinate. The reactants were 6 g of butyl hydrogen ethylphosphonite, 4.9 g of propyl bromide, and 1.4 g (an excess) of sodium. The constants of the butyl ethylpropylphosphinate were as follows: b.p. 83-84° (0.5 mm); d_4^{20} 0.9461; n_D^{20} 1.4381.

Found: MR 53.36
$C_9H_{21}PO_2$. Calculated: MR 53.50
Found %: P 16.27; 16.15
$C_9H_{21}PO_2$. Calculated %: P 16.12

The yield of ester was 5.1 g (66%).

9. Butyl Ethylisopropylphosphinate. Butyl ethylisopropylphosphinate was synthesized from 5 g of butyl hydrogen ethylphosphonite, 4.1 g of isopropyl bromide, and 1.6 g (an excess) of sodium. This synthesis, unlike those previously described, was carried out not in diethyl ether, but in gasoline of b.p. 80-120°, since the reaction did not go in ether. The butyl ethylisopropylphosphinate obtained in this way had the following constants: b.p. 70-72° (0.5 mm); d_4^{20} 0.9452; n_D^{20} 1.4365.

Found: MR 53.23
$C_9H_{21}PO_2$. Calculated: MR 53.50
Found %: P 15.85; 16.05
$C_9H_{21}PO_2$. Calculated %: P 16.12

The yield was 1.7 g (26%).

10. Butyl Butylethylphosphinate. The reactants were 8 g of butyl hydrogen ethylphosphonite, 7.8 g of butyl bromide, and 1.6 g (an excess) of sodium. The principal constants of the ester were: b.p. 89-90° (0.5 mm); d_4^{20} 0.9372; n_D^{20} 1.4400.

Found: MR 57.98
$C_{10}H_{23}PO_2$. Calculated: MR 58.01
Found %: P 15.12; 15.22
$C_{10}H_{23}PO_2$. Calculated %: P 15.02

The yield of the ester was 7.8 g (71%).

11. Butyl Decylethylphosphinate. The reactants were 3.4 g of butyl hydrogen ethylphosphonite, 5 g of decyl bromide, and 0.9 g (an excess) of sodium. The constants of the ester obtained were as follows: b.p. 148-150° (1.5 mm); d_4^{20} 0.9083; n_D^{20} 1.4489.

Found: MR 85.75
$C_{16}H_{35}PO_2$. Calculated: MR 85.82
Found %: P 10.88
$C_{16}H_{35}PO_2$. Calculated %: P 10.67

The yield was 3.4 g (54%).

12. Butyl Benzylethylphosphinate. The reactants were 3.5 g of butyl hydrogen ethyl phosphonite, 4 g of benzyl bromide, and 0.8 g (an excess) of sodium. The constants of the ester were: b.p. 124-125° (0.5 mm); d_4^{20} 1.0397; n_D^{20} 1.5050.

Found : MR 69.14

$C_{13}H_{21}PO_2$. Calculated : MR 69.37

Found % : P 12.78; 13.05

$C_{13}H_{21}PO_2$. Calculated % : P 12.89

The yield was 4.1 g (71%).

13. Isobutyl Ethylhexylphosphinate. The reactants were 3.5 g of isobutyl hydrogen ethylphosphonite, 0.5 g of hexyl iodide, and 0.7 g (an excess) of sodium. The principal constants of the ester were : b.p. 106-107° (0.5 mm); d_4^{20} 0.9235; n_D^{20} 1.4413.

Found : MR 67.05

$C_{12}H_{27}PO_2$. Calculated : MR 67.35

Found % : P 13.36; 13.39

$C_{12}H_{27}PO_2$. Calculated % : P 13.24

The yield was 2.5 g (51%).

14. Hexyl Ethylmethylphosphinate. The reactants were 5.6 g of hexyl hydrogen ethylphosphonite, 4.5 g of methyl iodide, and 1.1 g (an excess) of sodium. The principal constants of the ester were: b.p. 132-134° (12 mm); d_4^{20} 0.9483; n_D^{20} 1.4391.

Found: MR 53.22

$C_{10}H_{23}PO_2$. Calculated: MR 53.51

Found % : P 16.22; 16.37

$C_{10}H_{23}PO_2$. Calculated % : P 16.12

The yield was 3.3 g (51%).

15. Heptyl Diethylphosphinate. The reactants were 5.5 g of heptyl hydrogen ethylphosphonite, 4.2 g of ethyl iodide, and 1.0 g (an excess) of sodium. The principal constants of the ester were: b.p. 106-107° (0.5 mm); d_4^{20} 0.9332; n_D^{20} 1.4433.

Found : MR 62.63

$C_{11}H_{25}PO_2$. Calculated : MR 62.74

Found % : P 14.12; 14.27

$C_{11}H_{15}PO_2$. Calculated % : P 14.07

The yield was 3.4 g (53%).

16. Heptyl Ethylpropylphosphinate. The reactants were 5.7 g of heptyl hydrogen ethylphosphonite, 3.6 g of propyl bromide, and 1.2 g (an excess) of sodium. The constants of the ester were: b.p. 111-113° (0.5 mm); d_4^{20} 0.9662; n_D^{20} 1.4438.

Found : MR 67.18

$C_{12}H_{27}PO_2$. Calculated : MR 67.36

Found % : P 13.19; 13.37

$C_{12}H_{27}PO_2$. Calculated % : P 13.22

Yield was 4.2 g (60%).

17. Octyl Butylethylphosphinate. The reactants were 6 g of octyl hydrogen ethylphosphonite, 5.4 g of butyl iodide, and 0.9 g (an excess) of sodium. The principal constants of the ester were: b.p. 133-134° (1 mm); d_4^{20} 0.9159; n_D^{20} 1.4467.

Found : MR 76.49

$C_{14}H_{31}PO_2$. Calculated : MR 76.59

Found % : P 11.63; 11.74

$C_{14}H_{31}PO_2$. Calculated % : P 11.81

The yield was 3.3 g (40%).

18. Nonyl Benzylethylphosphinate. The reactants were 3.4 g of nonyl hydrogen ethylphosphonite, 2.6 g

of benzyl bromide, and 0.8 g (an excess) of sodium. The constants of the ester obtained were: b.p. 164-166° (0.5 mm); d_4^{20} 0.9814; n_D^{20} 1.4948.

Found : MR 92.20
$C_{18}H_{31}PO_2$. Calculated : MR 92.30
Found % : P 9.63; 9.68
$C_{18}H_{31}PO_2$. Calculated % : P 9.99

The yield was 2.5 g (52%).

19. Nonyl Decylethylphosphinate. The reactants were 4.5 g of nonyl hydrogen ethylphosphonite, 4.6 g of decyl bromide, and 0.9 g (an excess) of sodium. The principal constants of the ester were : b.p. 181-182° (0.5 mm); d_4^{20} 0.8947; n_D^{20} 1.4521.

Found : MR 108.74
$C_{21}H_{45}PO_2$. Calculated : MR 108.91
Found % : P 8.51; 8.64
$C_{21}H_{45}PO_2$. Calculated % : P 8.6

The yield was 4.5 g (61%).

SUMMARY

1. Is has been shown that acid esters of ethylphosphonous acid, like those of phosphorous acid, react with sodium to give sodium derivatives.

2. When sodium alkyl ethylphosphonites react with alkyl halides, alkylethylphosphinic esters are obtained.

Received January 16, 1954

A. E. Arbuzov Chemical Institute of the Kazan
Affiliated Institute of the USSR Academy of
Sciences

LITERATURE CITED

[1] B. A. Arbuzov and N. I. Rizpolozhensky, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1952, No. 5, 956.*

[2] B. A. Arbuzov and N. I. Rizpolozhensky, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1952, No. 5, 854.**

[3] A. E. Arbuzov, Thesis, St. Petersburg, 1905

[4] A. I. Razumov and O. A. Mukhacheva, Proc. Acad. Sci. USSR, 91, No. 2, 271 (1953).

[5] A. Michaelis, Th. Becker, Ber. 30, 1003 (1897).

[6] G. M. Kosolapoff, R. M. Watson, J. Am. Chem. Soc. 73, 4101 (1951).

---

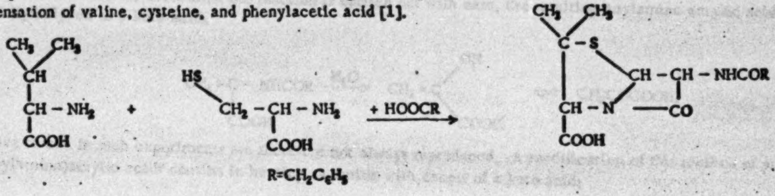
* See Consultants Bureau Translation, p. 843.
** " " " " 765

REACTIONS OF MERCAPTO AMINO ACIDS

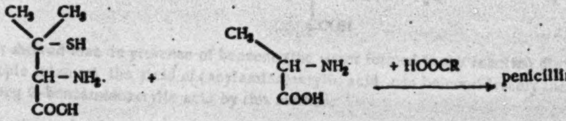
COMMUNICATION 4. N-ACYL-2,3-DIHALOALANINES

O. V. Kildisheva, L. P. Rasteikene, and I. L. Knunyants

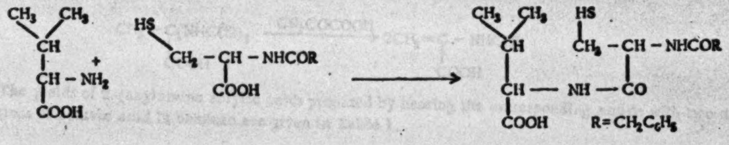
The search for antibiotics of the penicillin type has taken a new direction. Penicillin is a peculiar peptide, built up from several amino acids, and it is not altogether improbable that it is formed as a result of the enzymic condensation of valine, cysteine, and phenylacetic acid [1].



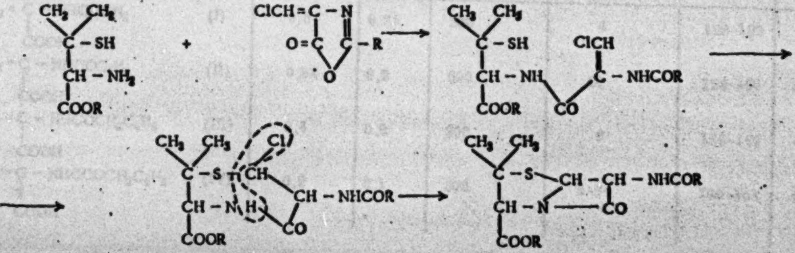
or, although this is less probable, of 3,3-dimethylcysteine, alanine, and phenylacetic acid



The coupling together of amino acids may be a promising line of approach to the synthesis of substances of the penicillin type. Recently, for example, a compound having an antibiotic activity of 12 units per mg has been obtained by the condensation of N-(phenylacetyl)-L-cysteine with D-valine [2].



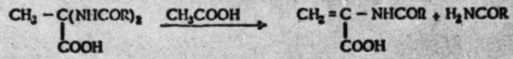
In spite of the negative results of numerous investigations on the synthesis of penicillin, the problem of synthesizing this antibiotic cannot be regarded as insoluble. It is quite obvious that the final stage of its synthesis must be a process in which the conditions are such as to ensure the survival of the penicillin formed. Such a process might be provided by the reaction of 3,3-dimethylcysteine and its derivatives with 2-benzyl (or phenyl)-4-(halomethylene)-2-oxazolin-5-ones.



However, it has not yet been found possible to carry out this reaction. At present only one such oxazolinone is known, namely 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one, which has been prepared by the action of thionyl chloride on the difficultly accessible 4-(hydroxymethylene)-2-phenyl-2-oxazolin-5-one [3]. The simplest method of preparing oxazolinones of this type would appear to be the dehydration of 2-(acylamino)-haloacrylic acids.

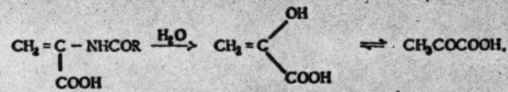
With a view to the preparation of various 2-(acylamino)-3-haloacrylic acids, methods of preparing 2-(acylamino) acrylic acids have been investigated and their properties have been studied. 2-(Acylamino)acrylic acids containing the following acylamino groups are now known: formamido [4, 5], acetamido [6], chloroacetamido [6,7], propionamido [8], benzamido [9-11], 2-phenacetamido [11-14], and benzyloxycarbonylamino [5].

A general method for the preparation of 2-(acylamino)acrylic acids consists in heating solutions of 2,2-bis(acylamino)propionic acids in glacial acetic acid:

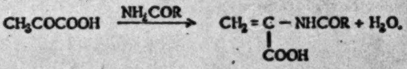


$$CH_3-\underset{COOH}{\underset{|}{C}}(NHCOR)_2 \xrightarrow{CH_3COOH} CH_2=\underset{COOH}{\underset{|}{C}}-NHCOR+H_2NCOR$$

It should be noted that, even when the reaction is carried out with care, the resulting acylamino acrylic acid is sometimes hydrolyzed to a keto acid:



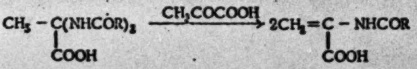
Positive results in such experiments are therefore not always reproduced. A modification of this method of preparing 2-(acylamino)acrylic acids consists in heating an amide with excess of a keto acid:



$$CH_3COCOOH \xrightarrow{NH_2COR} CH_2=\underset{COOH}{\underset{|}{C}}-NHCOR+H_2O.$$

In 1946 L. Kraft showed that in presence of benzene (the water formed in the reaction distils over with the benzene as an azeotropic mixture) the yield of (acylamino)acrylic acid can be considerably increased, but he did not succeed in preparing 2-benzamidoacrylic acid by this method.

Investigation has shown that by variation in the amount of solvent and the duration of heating any 2-(acylamino)acrylic acid can be prepared by this method. The by-product of this reaction, the 2,2-bis(acylamino)propionic acid, can itself be converted into the 2-acylamino)acrylic acid by being heated with excess of the keto acid in benzene:



$$CH_3-\underset{COOH}{\underset{|}{C}}(NHCOR)_2 \xrightarrow{CH_3COCOOH} 2CH_2=\underset{COOH}{\underset{|}{C}}-NHCOR$$

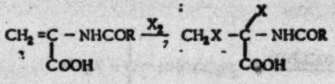
The yields of 2-(acylamino acrylic acids prepared by heating the corresponding amide with two molecular proportions of pyruvic acid in benzene are given in Table 1.

TABLE 1

2-(Acylamino)acrylic acid		Prepared from			Duration of heating (hours)	M.p. (°C)	Yield (%)
		$CH_3COCOOH$ (moles)	$RCONH_2$ (moles)	benzene (ml)			
$CH_2=\underset{COOH}{\underset{|}{C}}-NHCOCH_3$	(I)	0.5	0.25	500	4	198-199	53
$CH_2=\underset{COOH}{\underset{|}{C}}-NHCOC_6H_5$	(II)	0.46	0.2	600	20	158-160	30-35
$CH_2=\underset{COOH}{\underset{|}{C}}-NHCOCH_2C_6H_5$	(III)	0.4	0.2	300	6	189-190	40-50
$CH_2=\underset{COOH}{\underset{|}{C}}-NHCOOCH_2C_6H_5$	(IV)	0.2	0.1	300	2-3	100-101	43

The double bond of 2-(acylamino)acrylic acids has not lost its power of taking part in addition reactions. For example, in presence of peroxide catalysts 2-(acylamino)acrylic acids readily polymerize with formation of new polymers having unusual properties [5, 15, 16]. Esters of (acylamino)acrylic acids will polymerize even in absence of catalysts [10, 15-18]. 2-(Acylamino)acrylic acids are hydrogenated in presence of catalysts with formation of alanine derivatives [6, 19]. Amines add to them with formation of 2-(acyl amino)-3-(alkylamino)propionic acids [20, 21]. They unite with amides with formation of bis(acylamino)propionic acids [22, 23], and they react with diazomethane, which converts them into derivatives of pyrazolidinecarboxylic acid [6]*. The addition to 2-(acylamino)acrylic acids of hydrogen sulfide [10], thiols [24], and thioacetic acid [25, 26] has provided a practical means of preparing α-amino β-mercapto acids and their derivatives, such as lanthionine [27] and dimethyllanthionine [13]. 2-(Acylamino)acrylic acids unite readily also with hydrogen halides with formation of N-acyl-3-haloalanines, but their behavior towards the halogens has not been studied.

An investigation of the halogenation of 2-(acylamino)acrylic acids has shown that both chlorine and bromine readily add with formation of N-acyl-2,3-dihaloalanines in almost quantitative yields:

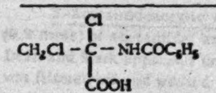
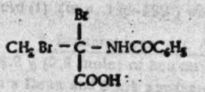
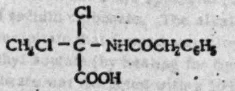
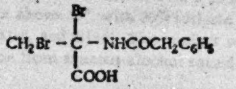
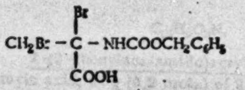


$$CH_2=\underset{COOH}{C}-NHCOR \xrightarrow{X_2} CH_2X-\underset{COOH}{\overset{X}{C}}-NHCOR$$

(V) X=Cl, R=C_6H_5; (VI) X=Br, R=C_6H_5; (VII) X=Cl R=$CH_2C_6H_5$; (VIII) X=Br, R=$CH_2C_6H_5$; (IX) X=Br, R=$OCH_2C_6H_5$.

Halogenation is effected readily at room temperature by means of 10% solutions of chlorine and bromine in dry chloroform or carbon tetrachloride. N-Acyl-2,3-dihaloalanines are insoluble in chloroform, but readily soluble in ether. They crystallize from ether as colorless needles having characteristic melting points (Table 2).

TABLE 2

N-Acyl-2,3-dihaloalanine		M.p. (°C)	Yield (%)
 $CH_2Cl-\underset{COOH}{\overset{Cl}{C}}-NHCOC_6H_5$	(V)	128-130 (decomp.)	98
 $CH_2Br-\underset{COOH}{\overset{Br}{C}}-NHCOC_6H_5$	(VI)	139-140 (decomp.)	93
 $CH_2Cl-\underset{COOH}{\overset{Cl}{C}}-NHCOCH_2C_6H_5$	(VII)	105-107 (decomp.)	93
 $CH_2Br-\underset{COOH}{\overset{Br}{C}}-NHCOCH_2C_6H_5$	(VIII)	128-130 (decomp.)	72
 $CH_2Br-\underset{COOH}{\overset{Br}{C}}-NHCOOCH_2C_6H_5$	(IX)	109-112 (decomp.)	96

It was found that the N-acyl-2,3-dihaloalanines obtained were extremely reactive. When the N-acyl-2,3-dibromoalanines were given prolonged treatments with water or aqueous alkaline solutions, complete hydrolysis occurred with formation of ammonium bromide. Heating for a short time with dilute alkali was sufficient to remove bromine completely, and the bromine could then be titrated quantitatively by the Volhard method. The dichloro acids were found to be more stable than the dibromo compounds; under the same conditions only one chlorine atom was removed, the second being hydrolyzed only after prolonged heating.

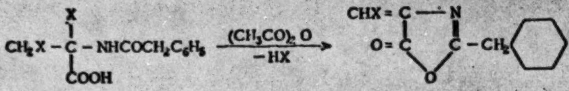
Acid hydrolysis of N-benzoyl-2,3-dibromoalanine (VI) and 2,3-dibromo-N-(phenylacetyl)alanine (VIII) resulted in the formation of different keto acids depending on the conditions. After a short hydrolysis addition of 2,4-dinitrophenylhydrazine precipitated the 2,4-dinitrophenylhydrazones of the previously unknown (benzoyloxy)- and (phenylacetoxy)-pyruvic acids (X and XI), m.p. 169-171° (decomp.) and 168-173° (decomp), respectively.

Longer hydrolysis of either compound resulted in the formation of hydroxypyruvic acid, which was isolated in the form of its known 2,4-dinitrophenylhydrazone, m.p. 160-161° [28]. The mechanism by which these keto acids were formed was elucidated by a study of the properties of N-acyl-3-halo-2-hydroxyalanines**. Further investigation of the properties of N-acyl-2,3-dihaloalanines showed that, when 2,3-dichloro- and 2,3-dibromo-N-(phenylacetyl) alanines were heated in carbon tetrachloride or chloroform solution with acetic anhydride, reaction readily occurred with evolution of HCl or HBr and formation of the previously unknown 2-benzyl-4-(chloromethylene)-2-oxazolin-5-one (XII) and the corresponding bromomethylene compound (XIII):

---

* 2-(2-Phenylacetamido)acrylic acid reacts normally with the theoretical amount of diazomethane at a low temperature, the corresponding ester being formed [14].

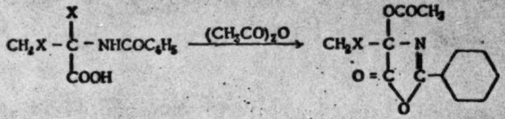
** See Communication 5 in this issue.



(XII) X = Cl, M.p. 114-115° (decomp.)
(XIII) X = Br, M.p. 112-114° (decomp.)

A convenient method has thus been found for the preparation of difficultly accessible unsaturated 2-benzyloxazolinones.

It was found, unexpectedly, that N-benzoyl-2,3-dihaloalanines, unlike the N-(phenylacetyl) compounds, were converted by reaction under the same conditions into stable saturated 4-acetoxy-4-(halomethyl)-2-phenyl-2-oxazolin-5-ones (XIV) and (XV):



(XIV) X = Br, M.p. 137-138°,
(XV) X = Cl, M.p. 110°.

A separate communication will be devoted to a study of the properties of the oxazolinones obtained.

EXPERIMENTAL

2-Acetamidoacrylic Acid (I). A mixture of 35 g (0.4 mole) of freshly distilled anhydrous pyruvic acid, 12 g (0.2 mole) of acetamide, and 300 ml of absolute benzene was boiled with simultaneous distillation of benzene in a Dean and Stark apparatus until the separation of water ceased (four hours). The crystalline precipitate that formed was filtered off and washed with ether. The 2-acetamidoacrylic acid was extracted with acetone. The yield of the acid (I) (m.p. 198-199°) was 14 g (53%).

2-Benzamidoacrylic Acid (II). A mixture of 40 g (0.46 mole) of freshly distilled anhydrous pyruvic acid, 24.2 g (0.2 mole) of benzamide, and 600 ml of absolute benzene was boiled with simultaneous distillation of benzene in a Dean and Stark apparatus (about 14 hours). The benzene solution was filtered and extracted with a 10% solution of sodium carbonate. The alkaline solution was separated and acidified to Congo Red with 30% sulfuric acid. The precipitate that formed was filtered off, washed with water, dried, and then dissolved in three times its amount of ethyl acetate (by heating for five minutes). The undissolved bis(benzamido)propionic acid was filtered off, and the filtrate was extracted with a 10% solution of sodium carbonate. The alkaline solution was acidified to Congo Red at not above 10° with 30% sulfuric acid, and the precipitate that formed was filtered off, washed repeatedly with water, and dried. The product was 11.5 g (30%) of 2-benzamidoacrylic acid melting at 150-152°. Recrystallization from aqueous alcohol raised the melting point to 158-160°.

Found %: C 62.72; H 4.82; N 7.95
$C_{10}H_9O_3N$. Calculated %: C 62.8; H 4.72; N 7.93

2-(2-Phenylacetamido)acrylic Acid (III). a) A mixture of 35 g (0.4 mole) of freshly distilled anhydrous pyruvic acid, 27 g (0.2 mole) of 2-phenylacetamide, and 300 ml of absolute benzene was boiled under the conditions described above for six hours. The crystalline precipitate that formed was filtered off, washed with ether and with glacial acetic acid (to remove the bis(2-phenylacetamido)propionic acid by-product), and then washed again with ether.

The yield of 2-(2-phenylacetamido)acrylic acid, m.p. 178-180°, was 50-60%. After repeated recrystallization of the acid from aqueous alcohol its melting point was 189-190°.

Found %: C 64.91; H 5.47
$C_{11}H_{11}O_3N$. Calculated %: C 64.4; H 5.36

2-(2-Phenylacetamido)acrylic acid is readily soluble in alcohol and acetone, and can be crystallized from isoproyl alcohol or aqueous acetone.

b) A mixture of 17.6 g (0.2 mole) of pyruvic acid, 34.0 g (0.1 mole) of bis(2-phenylacetamido)propionic acid, and 135 ml of absolute benzene was boiled in a Dean and Stark apparatus for 18 hours. The crystalline precipitate was filtered off and purified as in the preceding experiment. The product was 24.5 g (59%) of 2-(2-phenylacetamido) acrylic acid, m.p. 174-176°.

2-(Benzyloxycarbonylamino)acrylic Acid (IV). Benzyl carbamate $NH_2COOCH_2C_6H_5$ was prepared either by the action of ammonia on benzyl chloroformate [29] or by the condensation of urea with benzyl alcohol in presence of stannic chloride [30]. A mixture of 17.6 g (0.2 mole) of freshly distilled anhydrous pyruvic acid, 15.1 g (0.1 mole) of benzyl carbamate, and 300 ml of absolute benzene was boiled under the conditions described above for three hours. The benzene solution was extracted with a saturated solution of sodium bicarbonate, and the unchanged benzyl carbamate (3.4 g) was filtered off. The alkaline solution was extracted with 50 ml of ether and acidified to Congo Red with concentrated hydrochloric acid. The oil that separated quickly solidified, and was then filtered off, washed with a small amount of water, and dried in a vacuum desiccator over P_2O_5. The product was 9.5 g (43%) of 2-(benzyloxycarbonylamino)acrylic acid, m.p. 100-101° (from benzene)[*].

Found %: C 60.2; H 4.96

$C_{11}H_{11}O_4N$. Calculated %: C 59.72; H 5.0

When the same reaction was carried out with equimolecular amounts of reactants, bis(benzyloxycarbonylamino)-propionic acid of m.p. 134-136° (from 70% alcohol) was formed quantitatively.

2-(Benzyloxycarbonylamino)acrylic acid is readily soluble in alcohol, ether, and chloroform; it may be crystallized from aqueous alcohol, benzene, and toluene. When treated with acids and alkalis, it decomposes rapidly with formation of benzyl carbamate. It polymerizes when kept for a long time.

N-Benzoyl-2,3-dichloroalanine (V). Under cooling with ice water, 9.6 g (0.05 mole) of 2-benzamidoacrylic acid was treated with excess of chlorine dissolved in carbon tetrachloride (7.1 g of chlorine in 71 ml of carbon tetrachloride). Reaction proceeded with appreciable evolution of heat, and after 1-2 minutes a crystalline precipitate began to form in the clear solution. After an hour the precipitate was filtered off, washed, and dried. The product was 13.1 g (98%) of N-benzoyl-2,3-dichloroalanine, and after recrystallization from absolute ether is melted at 128-130° with decomposition. N-Benzoyl-2,3-dichloroalanine is a stable colorless crystalline compound. It is readily soluble in absolute ether, but insoluble in chloroform and carbon tetrachloride. A mixture of 0.1035 g of N-benzoyl-2,3-dichloroalanine, 15 ml of ethanol, and 2 g of sodium was boiled for one hour, after which the solution was cooled and diluted with water. The solution was acidified with concentrated nitric acid, and halogen was determined by Volhard titration.

Found %: Cl 27.0

$C_{10}H_9O_3NCl_2$. Calculated %: Cl 27.1

A weighed amount of N-benzoyl-2,3-dichloroalanine was dissolved in 0.5 N NaOH, and after one hour the solution was acidified with concentrated nitric acid and the halogen determined by Volhard titration.

Found %: Cl 15.6

$C_{10}H_8O_3NCl$. Calculated %: Cl 15.8

N-Benzoyl-2,3-dibromoalanine (VI). 2-Benzamidoacrylic acid (11.4 g, i.e. 0.06 mole) was dissolved in 96 ml of chloroform containing 9.6 g (0.06 mole) of bromine. Reaction occurred with appreciable evolution of heat, and after 1-2 minutes a crystalline precipitate began to form in the clear solution[**]. After 30 minutes the precipitate was filtered off, washed with dry chloroform, and dried in a vacuum desiccator over phosphoric oxide. The product was 19.5g (93%) of N-benzoyl-2,3-dibromoalanine, which, after recrystallization from absolute ether, melted with decomposition at 139-140°. An accurately weighed amount of the dibromo acid was dissolved in 0.5 N NaOH at 50-60°. After 5-7 minutes the solution was cooled, acidified with concentrated nitric acid, and titrated by the Volhard method.

Found %: Br 43.7

$C_{10}H_9O_3NBr_2$. Calculated %: Br 45.6

N-Benzoyl-2,3-dibromoalanine is a stable colorless crystalline compound. When kept in a moist atmosphere, the acid decomposes with evolution of hydrogen bromide.

2,3-Dichloro-N-(phenylacetyl)alanine (VII). 2-(2-Phenylacetamido)acrylic acid (10.25 g, i.e. 0.05 mole) was treated with excess of chlorine by shaking it with a solution of 5.5 g of chlorine in 55 g of carbon tetrachloride. Chlorination occurred with appreciable evolution of heat. The reaction mixture was left at room temperature overnight, and on the next day the precipitate was filtered off, washed with chloroform, and dried. The yield of 2,3-dichloro-N-(phenylacetyl)alanine was 12.75g (93%), and after recrystallization from absolute ether it melted with decomposition at 105-107°. A mixture of 0.2100 g of 2,3-dichlor-N-(phenylacetyl)alanine, 15 ml of absolute alcohol, and 2 g of sodium was boiled for one hour and then cooled and diluted with water. After acidification of the solution with concentrated nitric acid, halogen was determined by Volhard titration.

---

[*] The acid (IV) has been prepared independently from 2,2-bis(benzyloxycarbonylamino)propionic acid; it melted at 105° [5].

[**] 2-Benzamidoacrylic acid may sometimes contain some bis(benzamido)propionic acid as impurity. The latter is quite insoluble in ether, and is readily removed when the N-benzoyl-2,3-dibromoalanine is crystallized from ether.

Found %: Cl 26.0
$C_{12}H_{11}O_3NCl_2$. Calculated %: Cl 25.7

2,3-Dibromo-N-(phenylacetyl)alanine (VIII). 2-(2-Phenylacetamido)acrylic acid (20.5 g, i.e. 0.1 mole) was treated with a solution of 16 g (0.1 mole) of bromine in 160 ml of chloroform. Bromination occurred with appreciable evolution of heat. The reaction mixture was left at room temperature overnight, and on the next day 20 ml of absolute ether was added and the mixture was refluxed with exclusion of moisture. The undissolved residue of bis(2-phenylacetamido)propionic acid, sometimes present as impurity, was filtered off, and the clear solution was set aside in a refrigerator. After 2-3 hours the crystalline precipitate that formed was filtered off, washed with dry chloroform, and dried in a vacuum desiccator over phosphoric oxide. The product was 20.5 g (73%) of 2,3-dibromo-N-(phenylacetyl) alanine, which formed colorless needles melting with decomposition at 128-130°.

An accurately weighed amount of the dibromo acid was dissolved in an excess of 0.5 N NaOH, and the solution was heated for five minutes at 50-60°. It was then cooled, acidified with concentrated nitric acid, and titrated for bromine by the Volhard method.

Found %: Br 42.9
$C_{12}H_{11}O_3NBr_2$. Calculated %: Br 43.8

In absence of moisture 2,3-dibromo-N-(phenylacetyl)alanine is a stable compound, readily soluble in ether and ethyl acetate, and almost insoluble in chloroform. It is readily decomposed by alcohol and by water, and when kept in a moist atmosphere it loses hydrogen bromide and is converted into 3-bromo-2-hydroxy-N-(phenylacetyl)alanine.

N-(Benzyloxycarbonyl)-2,3-dibromoalanine (IX). 2-(Benzyloxycarbonylamino)acrylic acid (9 g, i.e. 0.04 mole) was treated with a solution of 6.5 g (0.04 mole) of bromine in 65 ml of chloroform. Reaction occurred with evolution of heat, and after a few minutes a crystalline precipitate began to form in the clear solution. The reaction mixture was left in a refrigerator for 20 minutes, and the precipitate was then filtered off, washed with chloroform, and dried in a vacuum desiccator over phosphoric oxide. The yield of N-(benzyloxycarbonyl)-2,3-dibromoalanine was 14.8 g (96%); it melted with decomposition at 108-112°.

Found %: Br 41.4 (Volhard titration)
$C_{11}H_{11}O_4NBr_2$. Calculated %: Br 42

Bromine was determined as in the previous experiment. N-(Benzyloxycarbonyl)-2,3-dibromoalanine is insoluble in chloroform, benzene, and toluene, but very soluble in ether. It decomposes rapidly when kept in a moist atmosphere.

Acid Hydrolysis of N-Acyl-2,3-dibromoalanines

2,4-Dinitrophenylhydrazone of (Benzoyloxy)pyruvic Acid (X). N-Benzoyl-2,3-dibromoalanine (6.5 g, i.e. 0.018 mole) was dissolved at 55° in 100 ml of water. The solution was cooled, filtered, and treated with a 0.5% solution of 2,4-dinitrophenylhydrazine in 2 N HCl (800 ml). On the next day the crystalline precipitate was filtered off, washed with a small amount of water, and dried in a vacuum desiccator over phosphoric oxide. The yield of the 2,4-dinitrophenylhydrazone of (benzoyloxy)pyruvic acid, m.p. 168-173° (from alcohol), was 6.9 g (96.5%).

Found %: C 49.10; H 3.07
$C_{16}H_{12}O_8N_4$. Calculated %: C 49.4; H 3.09

2,4-Dinitrophenylhydrazone of (Phenylacetoxy)pyruvic Acid (XI). 2,3-Dibromo-N-(phenylacetyl)alanine (3.6 g, i.e. 0.01 mole) was warmed with 40 ml of water until dissolved (1-2 minutes), and the resulting solution was then rapidly cooled, filtered, and treated with a 0.5% solution of 2,4-dinitrophenylhydrazine in 2 N HCl (400 ml), when a yellow precipitate of the hydrazone was formed immediately. On the next day the precipitate was filtered off, washed with a small amount of water, and dried in a vacuum desiccator over phosphoric oxide. The yield of the 2,4-dinitrophenylhydrazone of (phenylacetoxy)pyruvic acid, m.p. 169-171° (from alcohol), was 3.85 g (95.8%).

Found %: C 50.5; H 3.3; N 15.1
$C_{17}H_{14}O_8N_4$. Calculated %: C 50.7; H 3.48; N 13.9

2,4-Dinitrophenylhydrazone of Hydroxypyruvic Acid. 2,3-Dibromo-N-(phenylacetyl)alanine (3.6 g, i.e. 0.01 mole) was warmed with 40 ml of water until dissolved (1-2 minutes at 70-80°). The solution was cooled and filtered, and was then left at room temperature for two days. The solution was evaporated down until crystallization began, the crystalline precipitate of phenylacetic acid was filtered off, and the mother liquor was evaporated to dryness. The dry residue was dissolved in 150 ml of water, and the resulting solution was filtered and treated with a 0.5% solution of 2,4-dinitrophenylhydrazine in 2 N HCl (400 ml). The mixture was left overnight in a refrigerator, and on the next day the hydrazone was filtered off, washed with a small amount of water, and dried in a vacuum desiccator over phosphoric oxide. The product was 0.8 g (32%) of the 2,4-dinitrophenylhydrazone of hydroxypyruvic acid, m.p. 160-161° (from ethyl acetate). There was no depression in a mixture melting test with a sample of the 2,4-dinitrophenylhydrazone of hydroxypyruvic acid prepared by another method (from bromopyruvic acid [28]).

2-Benzyl-4-(chloromethylene)-2-oxazolin-5-one (XII). 2-(2-Phenylacetamido)acrylic acid (10 g, i.e 0.05 mole) was treated with a solution of 3.55 g of chlorine in 50 ml of carbon tetrachloride). The reaction mixture was shaken for 30 minutes at room temperature and then set aside overnight. On the next day 50 ml of acetic anhydride was added, and carbon tetrachloride was removed at 40-55° at a residual pressure of 50 mm, which was then reduced to 4 mm. Acetic anhydride was then distilled off until crystallization began. The residue was diluted with a little absolute ethanol and then filtered off. It was washed, first with a little absolute alcohol, and then with ether. The product was 6.5 g (58%) of 2-benzyl-4-(chloromethylene)-2-oxazolin-5-one, which formed yellowish needles, melting with decomposition at 114-115° after recrystallization from absolute alcohol.

Found %: C 60.22; H 3.72; N 6.44

$C_{11}H_8O_2NCl$. Calculated %: C 59.2; H 3.63; N 6.33

2-Benzyl-4-(chloromethylene)-2-oxazolin-5-one is readily soluble in chloroform and ether, may be crystallized from alcohol, and is insoluble in water. It slowly decomposes (in 2-3 months) when kept in a moist atmosphere. With pyridine and pyridine bases it gives a green-blue coloration characteristic of (halomethylene)oxazolinones.

2-Benzyl-4-(bromomethylene)-2-oxazolin-5-one (XIII). 2-(2-Phenylacetamido)acrylic acid (10 g, i.e. 0.05 mole) was brominated in the way described above for the substance (VIII). On the next day 50 ml of acetic anhydride was added to the reaction mixture. The procedure adopted for the isolation of the oxazolinone (XIII) was exactly the same as that adopted for the isolation of (XII). The yield of 2-benzyl-4-(bromomethylene)-2-oxazolin-5-one was 7 g (52%); it melted at 110-112° (from absolute ether). It was found that the oxazolinone could be purified also by dissolution in chloroform and addition of absolute alcohol until a turbidity appeared. Completely pure crystals of m.p. 112-114° were precipitated.

Found %: C 49.80; H 3.07; N 5.5; Br 30.02

$C_{11}H_8O_2NBr$. Calculated %: C 49.62; H 3.00; N 5.2; Br 30.07

The oxazolinone (XIII) is very soluble in chloroform and is readily soluble also in alcohol, ether, and ethyl acetate. It gives a bluish-violet color with pyridine. It is hydrolyzed by alkali with formation of 3-bromo-2-(2-phenylacetamido)acrylic acid, m.p. 173°.

4-Acetoxy-4-(bromomethyl)-2-phenyl-2-oxazolin-5-one (XIV). 2-Benzamidoacrylic acid (9.5 g, i.e. 0.05 mole) was treated with a solution of 8 g of bromine in 80 ml of chloroform. After 30 minutes 50 ml of acetic anhydride was added, and the mixture was distilled under reduced pressure at 50-60°. After the distillation, the crystalline residue was filtered off, washed with a small amount of absolute ether, and dried in a vacuum desiccator over phosphoric oxide. The product was 6.8 g of the oxazolinone (XIV), m.p. 137-138° (from absolute alcohol). A further 4.2 g of the oxazolinone was obtained from the mother liquor, and the total yield was 70%. An 80% yield of the oxazolinone (XIV) was obtained from crystalline N-benzoyl-2,3-dibromoalanine.

Found %: C 46.28; H 3.99; N 4.66; Br 25.56

$C_{12}H_{16}O_4NBr$. Calculated %: C 46.15; H 3.20; N 4.5; Br 25.6

The oxazolinone (XIV) can be readily crystallized from ether, ethanol, methanol, and acetic anhydride in the form of colorless needles. It is readily soluble in chloroform and dioxan , has limited solubility in ether, and is insoluble in water. It is stable to the action of alkalis. An ethereal solution of (XIV) remains unchanged after being shaken with 0.5 N NaOH for six hours. When, however, the substance was heated with 0.5 N NaOH at 80°, decomposition occurred; acidification did not give a precipitate of the corresponding acid, but treatment with a 0.5% solution of 2,4-dinitrophenylhydrazine in 2 N HCl yielded the 2,4-dinitrophenylhydrazone of (benzoyloxy)pyruvic acid, m.p. 168-170° (from alcohol), identical with the hydrazone (X).

When heated with 25% sulfuric acid, the oxazolinone (XIV) rapidly dissolved, and addition of a 0.5% solution of 2,4-dinitrophenylhydrazine in 2 N HCl yielded a precipitate of the 2,4-dinitrophenylhydrazone of (benzoyloxy)peruvic acid, m.p. 168-173°, undepressed by admixture of the hydrazone (X). 4-Acetoxy-4-(bromomethyl)-2-phenyl-2-oxazolin-5-one gave the characteristic hydroxamic reaction for anhydrides (red coloration with hydroxylamine and ferric chloride). When kept for 1-2 months it decomposed with separation of acetic acid and formation of a resin of unknown composition.

4-Acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one (XV). A mixture of 9.5 g (0.05 mole) of 2-benzamidoacrylic acid and a solution of 7 g (100% excess) of chlorine in 70 ml of carbon tetrachloride was shaken, with cooling (temperature not above 20-25°) for 30 minutes. Acetic anhydride (50 ml) was then added, and the mixture was heated under reduced pressure at 60-65°, the oxazolinone (XV) being isolated in the way described for the oxazolinone (XII). The crystalline precipitate was filtered off and washed with a small amount of absolute ether. The product was 4.6 g of the oxazolinone (XV), melting with decomposition at 110° (from absolute ethanol). A further 4.5 g was isolated from the mother liquor, and the total yield of (XV) was 68%. The oxazolinone (XV) is very soluble in chloroform and ether, and it crystallizes from methanol, ethanol, and acetic anhydride in the form of colorless needles.

Found %: C 53.4; H 3.96; Cl 13.29

$C_{12}H_{10}O_4NCl$. Calculated %: C 53.9; H 3.74; Cl 13.5

Special experiments showed that, even when heated for a long time, 4-acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one is not converted into 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one. When the oxazolinone (XV) was prepared from crystalline N-benzoyl-2,3-dichloroalanine, a 74% yield was obtained.

SUMMARY

1. The addition of halogen to 2-(acylamino)acrylic acids has yielded some previously unknown N-acyl-2,3-dihaloalanines, namely N-benzoyl-2,3-dibromoalanine, N-benzoyl-2,3-dichloroalanine, 2,3-dibromo-N-(phenylacetyl)alanine, 2,3-dichloro-N-(phenyl acetyl)alanine, and N-(benzyloxycarbonyl)-2,3-dibromoalanine.

2. It has been shown that in presence of acetic anhydride 2,3-dibromo(and dichloro)-N-(phenylacetyl)alanines are readily converted into 2-benzyl-4-(halomethylene)-2-oxazolin-5-ones, whereas under the same conditions N-benzoyl-2,3-dibromo(and dichloro)alanines yield stable 4-acetoxy-4-(halomethyl)-2-phenyl-2-oxazolin-5-ones.

LITERATURE CITED

[1] H. Arnstein, P. Grant, Biochem. J. 55, V (1953).

[2] T. Holly et al., J. Am. Chem. Soc. 74, 4534 (1952).

[3] Chemistry of Penicillin, Princeton, N. J., 1949, p. 545.

[4] M. Shive, G. Shive, J. Am. Chem. Soc. 68, 117 (1946).

[5] M. Frankel, M. Reichmann, J. Chem. Soc. 1952, 289.

[6] M. Bergmann, K. Grafe, Z. Phys. Chem. 187, 187 (1930).

[7] V. Price, J. Greenstein, J. biol. chem. 171, 447 (1947).

[8] M. Coover, J. Dickey, U. S. Pat. 2622074; C. A. 47, 9993 (1953).

[9] B. Nicolet, J. Am. Chem. Soc. 57, 1073 (1935).

[10] E. Fry, J. Org. Chem., 15, 438 (1950).

[11] Chemistry of Penicillin, Princeton, N. J., 1949, p. 749.

[12] J. King, McMillan, J. Am. Chem. Soc. 72, 833 (1950).

[13] O. Süs, Ann. 569, 158 (1950).

[14] M. Brenner, K. Rüfenacht, Helv. 36, 1832 (1953).

[15] E. Isaacs, H. Sudgeon, Brit. Pat. 57777 (1946); Chem. Abs., 42, 6581 (1948).

[16] E. Rotstein, J. Chem. Soc. 1949, 1968.

[17] R. Adams et al., J. Am. Chem. Soc. 72, 5080 (1950).

[18] E. Isaacs, H. Sudgeon, Brit. Pat. 2461383 (1949); Chem. Abs., 3238 (1949).

[19] E. Fry, J. Org. Chem. 14, 887 (1949).

[20] V. Price, J. Greenstein, J. biol. chem. 173, 337 (1948).

[21] J. Elger, J. Greenstein, Archiv. Biochem. 319, 467 (1948).

[22] D. Shemin, R. Herbst, J. Am. Chem. Soc. 60, 1954 (1938).

[23] A. Martell, R. Herbst, J. Org. Chem. 6, 876 (1941).

[24] R. Nicolett, Science 81, 181 (1935).

[25] H. Beringer, Ber. 81, 326 (1948).

[26] M. Farlow, J. Org. Chem. 176, 71 (1948).

[27] A. Schöbert, A. Wagner, Ber. 80, 379 (1947).

[28] D. Sprinsson, E. Chargraff, J. biol. chem. 164, 417 (1946).

[29] J. Tiele, F. Dent, Ann. 302, 257.

[30] A. Paquin, Z. Naturforschung, No. 1, 518 (1946); Chem. Abs. 42, 123 (1948).

Received April 9, 1954

N. D. Zelinsky Institute of Organic Chemistry of the USSR Academy of Sciences.

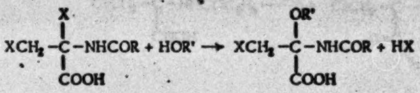
BLANK
PAGE

REACTIONS OF MERCAPTO AMINO ACIDS

COMMUNICATION 5. N-ACYL-3-HALO-2-HYDROXYALANINES AND THEIR DERIVATIVES

O. V. Kildisheva, M. G. Linkova, and I. L. Knunyants

In the preceding communication [1] we have described a method for the preparation of N-acyl-2,3-dihaloalanines and have shown that, whereas heating of N-benzoyl-2,3-dihaloalanines with acetic anhydride results in the formation of 4-acetoxy-4-(halomethyl)-2-phenyl-2-oxazolin-5-ones, 2,3-dihalo-N-(phenylacetyl)alanines yield 2-benzyl-4-(halomethylene)-2-oxazolin-5-ones under the same conditions. Further investigation of the properties of N-acyl-2,3-dihaloalanines has shown that they react readily with water and with alcohols, forming N-acyl-3-halo-2-hydroxyalanines (2-(acylamino)-3-halolactic acids) and N-acyl-2-alkoxy-3-haloalanines respectively (Table 1).



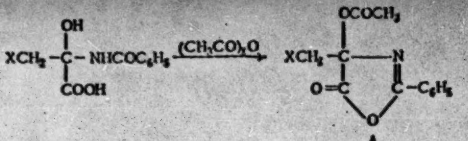
$$XCH_2-\overset{\overset{\displaystyle X}{|}}{\underset{\underset{\displaystyle COOH}{|}}{C}}-NHCOR + HOR' \rightarrow XCH_2-\overset{\overset{\displaystyle OR'}{|}}{\underset{\underset{\displaystyle COOH}{|}}{C}}-NHCOR + HX$$

(I) $X = Cl$, $R' = H$, $R = C_6H_5$; (V) $X = Cl$, $R' = H$, $R = CH_2C_6H_5$;
(II) $X = Cl$, $R' = CH_3$, $R = C_6H_5$; (VI) $X = Br$, $R' = H$, $R = CH_2C_6H_5$;
(III) $X = Cl$, $R' = C_2H_5$, $R = C_6H_5$; (VII) $X = Br$, $R' = C_2H_5$, $R = CH_2C_6H_5$.
(IV) $X = Br$, $R' = H$, $R = C_6H_5$;

The most convenient method for the preparation of N-acyl-3-halo-2-hydroxyalanines is the treatment of N-acyl-2,3-dihaloalanines with an aqueous solution of an equimolecular proportion of sodium bicarbonate. When kept in a moist atmosphere and when treated with alkalis or acids, N-acyl-3-halo-2-hydroxyalanines are readily hydrolyzed with formation of ammonium halide. Alkaline solutions of these acids give a reddish-violet color with ferric chloride, a reaction that is characteristic of hydroxypyruvic acid. As in the case of N-acyl-2,3-dihaloalanines, the chloro acid is more stable than the bromo acid. Thus, when an N-acyl-3-bromo-2-hydroxyalanine is treated with an excess of sodium bicarbonate, or is allowed to stand in acid solution, decomposition readily occurs. Treatment of the acid hydrolyzates with 2,4-dinitrophenylhydrazine gives hydrazones identical with the 2,4-dinitrophenylhydrazones of (benzoyloxy)- and (phenylacetoxy)-pyruvic acids already prepared from N-acyl-2,3-dibromoalanines [1]. On the other hand, N-acyl-3-chloro-2-hydroxyalanines can be reprecipitated with acid from solutions of their sodium salts without decomposition. As a rule, both the bromo and the chloro acids are very soluble in organic solvents, but great losses are suffered when they are purified by recrystallization. When N-acyl-3-halo-2-hydroxyalanines are treated with not more than the theoretical amount of diazomethane, it is possible to obtain the corresponding methyl esters, but the yields are not high. When excess of diazomethane is used, the acylamino group is eliminated quantitatively as an amide.

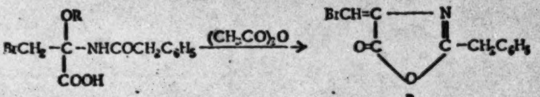
When treated with alcohols, N-acyl-2,3-dihaloalanines are immediately converted into N-acyl-2-alkoxy-3-haloalanines ((II), (III), and (VII) in the table). The latter compounds are more stable than the N-acyl-3-halo-2-hydroxyalanines: they are precipitated without decomposition from aqueous solutions of their sodium salts and can be crystallized unchanged from alcohols. They are converted quantitatively into the corresponding methyl esters by diazomethane ((X) and (XI) in the table). Further investigation has shown that heating of N-benzoyl-3-halo-2-hydroxyalanines with acetic anhydride results in the formation of the 4-acetoxy-4-(halomethyl)-2-phenyl-2-oxazolin-5-ones (XII) and (XIII), identical with the oxazolinones obtained by the action of acetic anhydride on N-benzoyl-2,3-dihaloalanines [1]. Under the same conditions, 3-halo-2-hydroxy(and alkoxy)-N-(phenylacetyl)alanines yield 2-benzyl-4-(halomethylene)-2-oxazolin-5-ones, identical with the oxazolinones obtained from 2,3-dihalo-N-(phenylacetyl)alanines: (See following page).

It has thus been established that, when acetic anhydride acts on N-acylalanines, different types (A and B) of oxazolinones are obtained, according to the identity of the acyl residue. Derivatives of N-banzoylalanine, such as N-benzoyl-2,3-dihalo- and N-benzoyl-3-halo-2-hydroxy-alanines, form only saturated oxazolinones of type A. On the other hand, derivatives of N-(phenylacetyl)alanine, whether they be 2,3-dihalo-, 3-halo-2-hydroxy-, or 2-alkoxy -3-halo-N-(phenylacetyl)alanines, form only unsaturated oxazolinones of type B. The question of whether or not the closure of the oxazolinone ring precedes the replacement of the 2-halo or 2-hydroxy by acetoxy was resolved



A

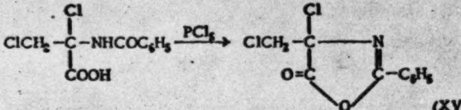
X=Cl (XII); X=Br (XIII)



B

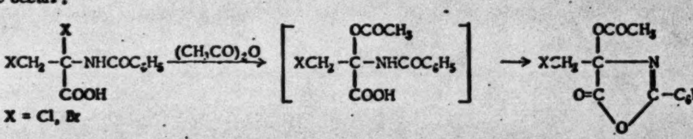
R=H, C_2H_5 (XIV)

by a study of the behavior of 4-chloro-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one (XV). This substance was readily prepared by the dehydration of N-benzoyl-2,3-dichloroalanine with the aid of phosphorus pentachloride:



(XV)

All attempts at converting the oxazolinone (XV) into 4-acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one or 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one (XVI) were unsuccessful. Whereas N-acyl-2,3-dihaloalanines are readily converted by the action of a saturated solution of sodium bicarbonate into 3-halo-2-hydroxy compounds, the oxazolinone (XV) is not affected under these conditions. When treated for a longer time with water, or when treated with methanol, opening of the oxazolinone ring occurs, and only then does replacement of the 2-halogen occur with formation of N-benzoyl-3-chloro-2-hydroxyalanine (I), or the methyl ester of N-benzoyl-3-chloro-2-methoxyalanine (X). The formation of 4-acetoxy-4-(halomethyl)-2-phenyl-2-oxazolin-5-one from N-benzoyl-2,3-dihaloalanines is therefore preceded by replacement of 2-halo by acetoxy, after which dehydration to the corresponding oxazolinone occurs:

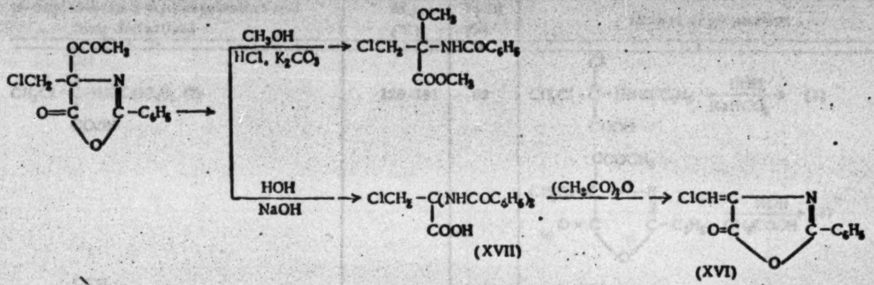


X = Cl, Br

These first (halomethyl)oxazolinones were found to be fairly stable compounds; they can, for example, be melted without decomposition, kept for 2-3 months when moisture is excluded, and crystallized without difficulty from glacial acetic acid, acetic anhydride, and even alcohol [1]. 4-Acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one can be crystallized without change from a mixture of acetic anhydride and pyridine and is not affected when heated to 150°. Acid hydrolysis of 4-acetoxy-4-(halomethyl)-2-phenyl-2-oxazolin-5-ones gave (benzoyloxy)pyruvic acid, which was isolated in the form of its 2,4-dinitrophenylhydrazone, identical with the hydrazone obtained from the product of the acid hydrolysis of N-acyl-2,3-dihaloalanines.

Hydrolysis with aqueous sodium bicarbonate or methanolic 2 N NaOH gave 2,2-bis(benzamido)-3-chloropropionic acid (XVII), which melted with decomposition at 140-141°. Unlike N-benzoyl-3-chloro-2-hydroxyalanines and 2-alkoxy-N-benzoyl-3-chloroalanines, (XVII) is readily converted into the known 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one (XVI) when heated with acetic anhydride: (See following page).

4-Acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one is hydrolyzed at room temperature by 80% acetic acid to N-benzoyl-3-chloro-2-hydroxyalanine. When it is treated with methanolic HCl or is heated with methanol in presence of very small amounts of potassium carbonate, the usual ester-formation reaction occurs, but, quite unexpectedly under these conditions, acetoxy is replaced by methoxy, and the product isolated is the methyl ester of N-benzoyl-3-chloro-2-methoxyalanine (X), identical with the ester obtained by the action of diazomethane on N-benzoyl-3-chloro-2-methoxyalanine.



EXPERIMENTAL

N-Benzoyl-3-chloro-2-hydroxyalanine (I). 1) N-Benzoyl-2,3-dichloroalanine (2.62 g, i.e. 0.01 mole) was vigorously agitated with a solution of 0.84 g (0.01 mole) of sodium bicarbonate in 9 ml of water. After ten minutes the precipitate formed was filtered off, washed with cold water, and dried over phosphoric oxide in a vacuum desiccator. The yield of N-benzoyl-3-chloro-2-hydroxyalanine (I), m.p. 111-114°, was 1.5 g (69%). The purification of the acid (I) by recrystallization from dichloroethane could be achieved only at the expense of great losses; m.p. 120-121° with a little decomposition.

Found %: C 49.2; H 4.07; N 5.47; Cl 14.14
$C_{10}H_{10}O_4NCl$. Calculated %: C 49.2; H 4.1; N 5.7; Cl 14.15

N-Benzoyl-3-chloro-2-hydroxyalanine is considerably more stable than the corresponding bromo acid; thus it can be reprecipitated with acids from aqueous solutions of its salts almost without loss and can be kept unchanged for a longer time.

2) 4-Acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one (0.26 g, i.e. 0.001 mole) was pasted with 1 ml of 90% acetic acid and left for three days at room temperature. After two days almost all of the precipitate had gone into solution, and the newly precipitated crystalline substance was filtered off, washed with a small amount of water, and dried. The product was 0.1 g of N-benzoyl-3-chlor-2-hydroxyalanine, m.p. 108-111° (with some decomposition), undepressed by admixture of some of the acid prepared from the dichloro acid.

N-Benzoyl-3-chloro-2-methoxyalanine (II). N-Benzoyl-2,3-dichloroalanine (2.6 g, i.e. 0.01 mole) was pasted with 3.5 ml of absolute methanol. The acid dissolved with noticeable evolution of heat, and after one minute a new crystalline precipitate formed. It was filtered off, washed with ether, and dried. The product was 2.0 g (78%) of N-benzoyl-3-chloro-2-methoxyalanine (II), m.p. 147-149° with decomposition. The acid (II) was dissolved in a saturated solution of sodium bicarbonate, and the solution was extracted with ether and then acidified with 25% sulfuric acid. The substance so obtained melted at 152-153°, raised by recrystallization from methanol to 159-160° (with decomposition).

Found %: C 50.84; H 4.88; Cl 13.85; N 5.4
$C_{11}H_{12}O_4NCl$. Calculated %: C 51.2; H 4.66; Cl 13.87; N 5.43

N-Benzoyl-3-chloro-2-ethoxyalanine (III). N-Benzoyl-2,3-dichloro-alanine (2.6 g, i.e. 0.01 mole) was dissolved in 1 ml of absolute ethanol. Reaction occurred with evolution of an appreciable amount of heat. After two hours at 0-4°, a crystalline precipitate formed. It was filtered off, washed with a little water, and dried. The N-Benzoyl-3-chloro-2-ethoxyalanine obtained melted with decomposition at 115-117°. Some more was obtained by addition of ice water to the alcoholic mother liquor (total yield 50%). The acid (III) was reprecipitated by acids from its solution in aqueous sodium bicarbonate, but it formed as an oil, which solidified only after the addition of some of the crystalline acid (III). The acid (III) is very soluble in ethanol, methanol, and ether, but it is insoluble in water. It melts with decomposition at 117-118° after recrystallization from absolute ether or acetic anhydride (when the latter is used, the temperature must not rise above 50°).

Found %: C 52.88; H 5.43; Cl 13.4
$C_{12}H_{14}O_4NCl$ Calculated %: C 53.04; H 5.15; Cl 13.07

N-Benzoyl-3-bromo-2-hydroxyalanine (IV). N-Benzoyl-2,3-dibromoalanine (12 g, i.e. 0.0032 mole) was agitated vigorously with a saturated solution of sodium bicarbonate (2.88 g, i.e. 0.032 mole, in 29 ml of water).

TABLE

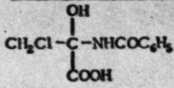
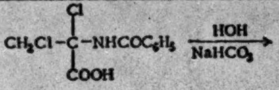
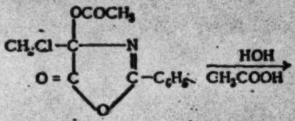
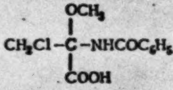
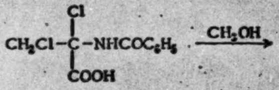
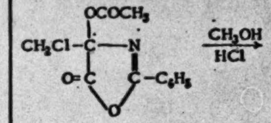
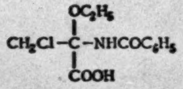
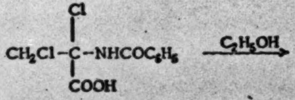
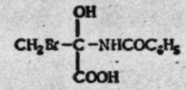
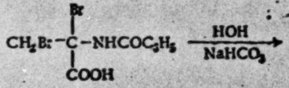
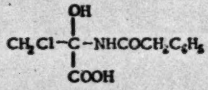
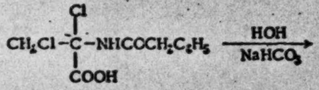
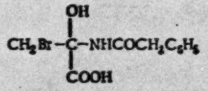
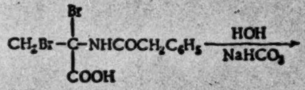
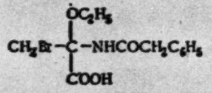
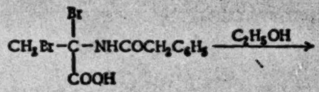
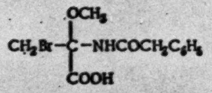
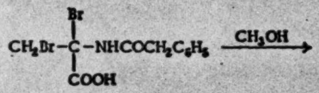
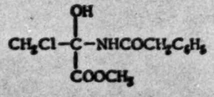
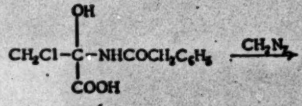
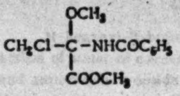
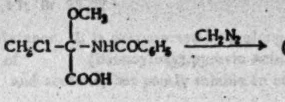
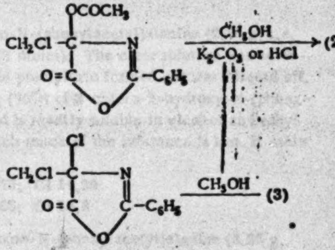
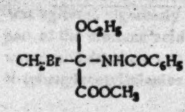
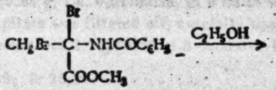
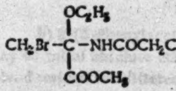
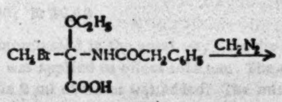
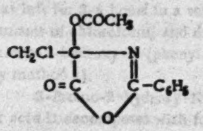
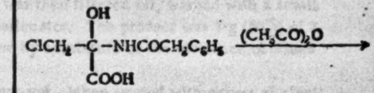
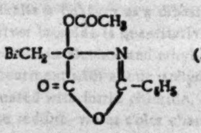
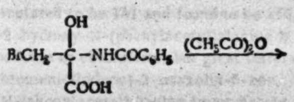
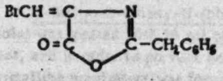
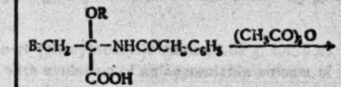
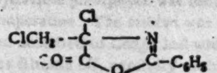
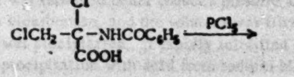
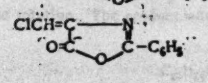
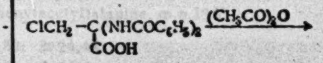
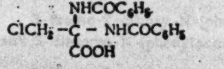
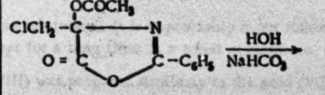
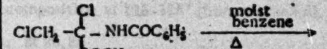
N-Acyl-3-halo-2-hydroxyalanines and their derivatives	M.p. (°C)	Yield (%)	Method of preparation
1	2	3	4
 $CH_2Cl-\overset{OH}{\underset{COOH}{C}}-NHCOC_6H_5$ (I)	120-121	69	 $CH_2Cl-\overset{Cl}{\underset{COOH}{C}}-NHCOC_6H_5 \xrightarrow[NaHCO_3]{HOH}$ (1)  (2)
 $CH_2Cl-\overset{OCH_3}{\underset{COOH}{C}}-NHCOC_6H_5$ (II)	159-160	78	 $CH_2Cl-\overset{Cl}{\underset{COOH}{C}}-NHCOC_6H_5 \xrightarrow{CH_3OH}$ (1)  (2)
 $CH_2Cl-\overset{OC_2H_5}{\underset{COOH}{C}}-NHCOC_6H_5$ (III)	117-118	50	 $CH_2Cl-\overset{Cl}{\underset{COOH}{C}}-NHCOC_6H_5 \xrightarrow{C_2H_5OH}$
 $CH_2Br-\overset{OH}{\underset{COOH}{C}}-NHCOC_6H_5$ (IV)	105-106	94	 $CH_2Br-\overset{Br}{\underset{COOH}{C}}-NHCOC_6H_5 \xrightarrow[NaHCO_3]{HOH}$
 $CH_2Cl-\overset{OH}{\underset{COOH}{C}}-NHCOCH_2C_6H_5$ (V)	105-106	70	 $CH_2Cl-\overset{Cl}{\underset{COOH}{C}}-NHCOCH_2C_6H_5 \xrightarrow[NaHCO_3]{HOH}$
 $CH_2Br-\overset{OH}{\underset{COOH}{C}}-NHCOCH_2C_6H_5$ (VI)	105-106	93	 $CH_2Br-\overset{Br}{\underset{COOH}{C}}-NHCOCH_2C_6H_5 \xrightarrow[NaHCO_3]{HOH}$
 $CH_2Br-\overset{OC_2H_5}{\underset{COOH}{C}}-NHCOCH_2C_6H_5$ (VII)	126	70	 $CH_2Br-\overset{Br}{\underset{COOH}{C}}-NHCOCH_2C_6H_5 \xrightarrow{C_2H_5OH}$
 $CH_2Br-\overset{OCH_3}{\underset{COOH}{C}}-NHCOCH_2C_6H_5$ (VIII)	125-126	–	 $CH_2Br-\overset{Br}{\underset{COOH}{C}}-NHCOCH_2C_6H_5 \xrightarrow{CH_3OH}$
 $CH_2Cl-\overset{OH}{\underset{COOCH_3}{C}}-NHCOCH_2C_6H_5$ (IX)	101-103	–	 $CH_2Cl-\overset{OH}{\underset{COOH}{C}}-NHCOCH_2C_6H_5 \xrightarrow{CH_2N_2}$

TABLE (Continued)

1	2	3	4
 $CH_2Cl-\overset{OCH_3}{\underset{COOCH_3}{C}}-NHCOC_6H_5$ (X)	105-106	quantitative	 $CH_2Cl-\overset{OCH_3}{\underset{COOH}{C}}-NHCOC_6H_5 \xrightarrow{CH_2N_2}$ (1)
		70	 $\xrightarrow[K_2CO_3\text{ or }HCl]{CH_3OH}$ (2) $\xrightarrow{CH_3OH}$ (3)
 $CH_2Br-\overset{OC_2H_5}{\underset{COOCH_3}{C}}-NHCOC_6H_5$	104-106	70	 $CH_2Br-\overset{Br}{\underset{COOCH_3}{C}}-NHCOC_6H_5 \xrightarrow{C_2H_5OH}$
 $CH_2Br-\overset{OC_2H_5}{\underset{COOCH_3}{C}}-NHCOCH_2C_6H_5$ (XI)	97-98	60	 $CH_2Br-\overset{OC_2H_5}{\underset{COOH}{C}}-NHCOCH_2C_6H_5 \xrightarrow{CH_2N_2}$
 (XII)	108-110		 $ClCH_2-\overset{OH}{\underset{COOH}{C}}-NHCOCH_2C_6H_5 \xrightarrow{(CH_3CO)_2O}$
 (XIII)	130		 $BrCH_2-\overset{OH}{\underset{COOH}{C}}-NHCOC_6H_5 \xrightarrow{(CH_3CO)_2O}$
 (XIV)	109-111 (decomp.)		 $BrCH_2-\overset{OR}{\underset{COOH}{C}}-NHCOCH_2C_6H_5 \xrightarrow{(CH_3CO)_2O}$ R = H, C_2H_5
 (XV)	70-74		 $ClCH_2-\overset{Cl}{\underset{COOH}{C}}-NHCOC_6H_5 \xrightarrow{PCl_5}$
 (XVI)	135-137	quantitative	 $ClCH_2-\underset{COOH}{C}(NHCOC_6H_5)_2 \xrightarrow{(CH_3CO)_2O}$
 $ClCH_2-\overset{NHCOC_6H_5}{\underset{COOH}{C}}-NHCOC_6H_5$ (XVII)	140-141		 $\xrightarrow[NaHCO_3]{HOH}$ (1)  $ClCH_2-\overset{Cl}{\underset{COOH}{C}}-NHCOC_6H_5 \xrightarrow[\Delta]{\text{moist benzene}}$ (2)

After 2-4 minutes the precipitate was filtered off, carefully washed with cold water, and dried over phosphoric oxide in a vacuum desiccator. The product was 8.7 g (94%) of N-benzoyl-3-bromo-2-hydroxyalanine, m.p. 105-106°.

Found %: C 41.93; H 3.73; Br 27.93
$C_{10}H_{10}O_4NBr$. Calculated %: C 41.66; H 3.47; Br 27.77

N-Benzoyl-3-bromo-2-hydroxyalanine is a colorless crystalline substance. It is decomposed by prolonged action of water or excess of sodium bicarbonate solution with formations of (benzoyloxy) pyruvic acid [1] and ammonium bromide. It is readily soluble in ethyl acetate, dioxan, and acetone, but poorly soluble in ether. Very great losses are suffered when it is crystallized from ethyl acetate.

3-Chloro-2-hydroxy-N-(phenylacetyl)alanine (V). 2,3-Dichloro-N-(phenylacetyl)alanine (2.76 g, i.e. 0.01 mole) was treated with a saturated solution of sodium bicarbonate (2 moles). The clear solution was acidified to Congo Red with 25% sulfuric acid. After ten minutes a crystalline precipitate formed. It was filtered off, washed with a small amount of water, and dried. The product was 1.8 g (70%) of 3-chloro-2-hydroxy-N-(phenylacetyl)alanine melting with some decomposition at 104-105°. The acid is readily soluble in alcohol and ethyl acetate. After recrystallization from ethyl acetate, in the course of which much of the substance is lost, it melts at 106-106.5°.

Found %: C 51.23; H 4.73; Cl 14.20
$C_{11}H_{12}O_4NCl$. Calculated %: C 51.26; H 4.66; Cl 13.8

3-Bromo-2-hydroxy-N-(phenylacetyl)alanine (VI). a) 2,3-Dibromo-N-(phenylacetyl)alanine (3.65 g, was agitated vigorously with a saturated solution of sodium bicarbonate (0.84 g, i.e. 0.01 mole, in 8 ml of water); part of the dibromo acid went into solution. After 3-5 minutes the precipitate was filtered off, carefully washed with water, and dried over phosphoric oxide in a vacuum desiccator. The product was 2.7 g (93%) of 3-bromo-2-hydroxy-N-(phenylacetyl)alanine, melting with decomposition at 103-104°.

Found %: C 43.01; H 4.38; Br 26.35
$C_{11}H_{12}O_4NBr$ Calculated %: C 43.7; H 4.00; Br 26.49

b) 2-(2-Phenylacetamido)acrylic acid (10 g, i.e. 0.05 mole) was brominated in the usual way. On the next day 40 ml of absolute ether was added to the reaction mixture, and heat was applied to effect solution. The undissolved residue was filtered off, and the filtrate was shaken vigorously while 2 ml of water was added. The mixture was left for 3-4 hours in a refrigerator, and the crystalline precipitate was then filtered off, washed with a small amount of chloroform, and dried over phosphoric oxide in a vacuum desiccator. The product was 7 g (50%) of 3-bromo-2-hydroxy-N-(phenylacetyl)alanine, m.p. 105-106°, undepressed by admixture of the substance obtained by method a).

3-Bromo-2-hydroxy-N-(phenylacetyl)alanine is an unstable compound. When treated with excess of alkali or acid it decomposes with formation of (phenylacetoxy)pyruvic acid and ammonium bromide. In titration with alkalis it behaves as a dibasic acid; the neutralization equivalent was calculated to be 151 and found to be 146. Silver bromide is quantitatively precipitated by 0.1 N $AgNO_3$. 3-Bromo-2-hydroxy-N-(phenylacetyl)alanine is very soluble in alcohol and ethyl acetate; it can be crystallized from dichloroethane or chloroform, but great losses occur. Treatment with acetic anhydride at 60-70° converts it into 2-benzyl-4-(bromomethylene)-2-oxazolin-5-one. When treated with ferric chloride, an alkaline solution of 3-bromo-2-hydroxy-N-(phenylacetyl)alanine immediately gives the reddish-violet color characteristic of hydroxypyruvic acid.

3-Bromo-2-ethoxy-N-(phenylacetyl)alanine (VII). 2,3-Dibromo-N-(phenylacetyl)alanine (3.65 g, i.e. 0.01 mole) was treated with 10 ml of absolute ethanol. The acid dissolved with evolution of an appreciable amount of heat, and in order to prevent decomposition the reaction mixture was cooled with ice water. After 1-2 minutes a crystalline precipitate was formed in the solution. The excess of alcohol was removed under reduced pressure at room temperature. The residue was dissolved in a saturated solution of sodium bicarbonate, and the solution was filtered and acidified to Congo Red with concentrated hydrochloric acid. An oil was precipitated. It rapidly solidified and was filtered off, carefully washed with water, and purified by repeated reprecipitation with acid from sodium bicarbonate solution. The product was 2.0 g (70%) of 3-bromo-2-ethoxy-N-(phenylacetyl)alanine, m.p.126°.

Found %: C 47.52; H 4.82; Br 24.48
$C_{13}H_{16}O_4NBr$ Calculated %: C 47.4; H 4.55; Br 24.3

3-Bromo-2-ethoxy-N-(phenylacetyl)alanine is a colorless crystalline substance. It is appreciably more stable than 2,3-dibromo-N-(phenylacetyl)alanine, but it is decomposed when kept for a long time in a moist atmosphere.

3-Bromo-2-methoxy-N-(phenylacetyl)alanine (VIII). The acid (VIII) was prepared similarly to the acid (VII), methanol being used in place of ethanol. The acid (VIII) melted with decomposition at 125-126° (from methanol).

Found %: C 45.16; H 4.51; Br 25.82
$C_{12}H_{14}O_4NBr$ Calculated %: C 45.6; H 4.42; Br 25.4

Methyl Ester of 3-Chloro-2-hydroxy-N-(phenylacetyl)alanine (IX). 3-Chloro-2-hydroxy-N-(phenylacetyl) alanine (2.5 g) was suspended in 10 ml of absolute ether and treated with the calculated amount of an ethereal solution of diazomethane. When the addition was complete, the solution was rapidly filtered and ether was removed until crystallization began. The product was a mixture of the methyl ester of 3-chloro-2-hydroxy-N-(phenylacetyl)-alanine and 2-phenylacetamide. It was difficult to separate, but after numerous fractional crystallizations from a mixture of three parts of ether and one of ethyl acetate we succeeded in obtaining the methyl ester of 3-chloro-2-hydroxy-N-(phenylacetyl)alanine, m.p. 101-103°;

	Found %:	C 52,78; H 5,20; Cl 13,20
$C_{12}H_{14}O_4NCl$.	Calculated %:	C 53,04; H 5,15; Cl 13,07

and 2-phenylacetamide, m.p. 156-158°, undepressed by admixture of known 2-phenylacetamide.

Methyl Ester of N-Benzoyl-3-chloro-2-methoxyalanine (X). 1) N-Benzoyl-3-chloro-2-methoxyalanine (0.267 g, i.e. 0.001 mole) was mixed with 5 ml of absolute ether, and an ethereal solution of diazomethane was added in presence of a little methanol. After removal of a part of the ether, the methyl ester of N-benzoyl-3--chloro-2-methoxyalanine m.p. 103°, was obtained in almost quantitative yield. After recrystallization from absolute ether it melted at 105-106°.

	Found %:	C 52,84; H 5,2; Cl 12,33
$C_{12}H_{14}O_4NCl$	Calculated %:	C 53,0; H 5,15; Cl 13,07

2) 4-Acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one (0.52 g, i.e. 0.002 mole) was mixed with 10 ml of methanol, 0.5 ml of a 10% solution of potassium carbonate was added, and the mixture was refluxed for 20 minutes. The mixture was then evaporated under reduced pressure to one-half of its original volume, 4 ml of water was added, and the mixture was set aside for 1-2 hours. The crystalline precipitate (0.36 g, i.e. 70%, of the methyl ester og N-benzoyl-3-chloro-2-methoxyalanine) was filtered off. Recrystallization from ether gave a product of m.p. 105-106°, undepressed by admixture of ester obtained by treatment of N-benzoyl-3-chloro-2-methoxyalanine with diazomethane.

3) 4-Acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one (2.67 g, i.e. 0.01 mole) was mixed with 10 ml of absolute methanol, and a catalytic amount of a saturated solution of hydrogen chloride in methanol was added. Reaction set in spontaneously with evolution of heat, and the oxazolinone went into solution. After partial evaporation of the methanol and cooling, a precipitate formed. It was filtered off, washed with water, and dried. The product was 2 g of a mixture of N-benzoyl-3-chloro-2-methoxyalanine and its methyl ester. In order to separate these the mixture was carefully ground with a 10% solution of sodium bicarbonate. The residue, filtered off, washed with water, and dried, was 1.3 g (50%) of the methyl ester of N-benzoyl-3-chloro-2-methoxyalanine, which melted, after recrystallization from methanol, at 104-105°. This ester was found to be identical with that obtained by the action of diazomethane on N-benzoyl-3-chloro-2-methoxyalanine. Careful acidification of the bicarbonate filtrate with N HCl under cooling with ice water yielded 0.4 g (15%) of an acid that melted with decomposition at 156-157° after recrystallization from methanol. There was no melting point depression in admixture with N-benzoyl-3-chloro-2-methoxyalanine obtained by the action of methanol on N-benzoyl-2,3-dichloroalanine.

Methyl Ester of N-Benzoyl-2,3-dibromoalanine. a) A mixture of 5.7 g of 2-benzamidoacrylic acid, 100 ml of methanol, 1 g of hydroquinone, 2 g of anhydrous sodium carbonate, and 8 g of dimethyl sulfate was refluxed for two hours. The mixture was cooled, and 200 ml of absolute ether was added. The precipitate that formed was filtered off, and the filtrate was evaporated under reduced pressure. The residue was again dissolved in absolute ether, and the solution was filtered and again evaporated. The yield of almost pure methyl 2-benzamidoacrylate was 3 g (50%). This ester could not be distilled, even in a vacuum: polymerization occurred at 150°. It was found that the 2-benzamidoacrylic ester absorbed the theoretical amount of bromine.

b) Methyl 2-benzamidoacrylate (1.0 g) was dissolved in 5 ml of absolute chloroform, and 16 ml of a 10% solution of bromine in chloroform was added in 5-ml portions. Reaction occurred with evolution of an appreciable amount of heat, and the bromine color rapidly disappeared. When addition of bromine was complete, the solution was evaporated under reduced pressure with exclusion of moisture. A theoretical yield was obtained of the methyl ester of N-benzoyl-2,3-dibromoalanine, m.p. 90-91° (from absolute ether). The ester is unstable and decomposes when kept in a moist atmosphere.

	Found %:	N 3,78; Br 42,3 (Volhard titration)
$C_{11}H_{11}O_3NBr_2$	Calculated %:	N 3,83; Br 43,8

Methyl Ester of N-Benzoyl-3-bromo-2-ethoxyalanine. The methyl ester of N-benzoyl-2,3-dibromoalanine (0.36 g, i.e. 0.001 mole) was added to 1 ml of ethanol. The ester rapidly went into solution, and a crystalline precipitate of 0.2 g (70%) of the methyl ester of N-benzoyl-3-bromo-2-ethoxyalanine, m.p. 104-106°, was formed.

Found %: C 47,25; H 4,44; Br 24,02; N 4,16
$C_{13}H_{16}O_4NBr$ Calculated %: C 47,27; H 4,84; Br 24,24; N 4,24

Methyl Ester of 3-Bromo-2-ethoxy-N-(phenylacetyl)alanine (XI). 3-Bromo-2-ethoxy-N-(phenylacetyl) alanine (0.5 g) was pasted with 2 ml of absolute ether, and an ethereal solution of diazomethane was added gradually. When the evolution of nitrogen ceased, the solution was filtered and placed in a refrigerator. A crystalline precipitate appeared after 10-15 minutes and was filtered off, washed with a small amount of absolute ether, and dried over phosphoric oxide in a vacuum desiccator. The product was 0.3 g of the methyl ester of 3-bromo-2-ethoxy-N-(phenylacetyl)alanine, m.p. 97-98°.

Found %: C 48,9; H 5,36; Br 22,85
$C_{14}H_{18}NO_4Br$ Calculated %: C 48,8; H 5,23; Br 23,2

4-Acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one (XII). A mixture of 2.25 g (0.01 mole) of N-benzoyl-3-chloro-2-hydroxyalanine and 5 ml of acetic anhydride was heated at 70-80° for ten minutes. The acetic anhydride was distilled off at 10 mm residual pressure, and the residue was washed with ether. The product was 1.4 g (50%) of 4-acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one, m.p. 107-108° (from absolute alcohol). A mixture test with a sample prepared from N-benzoyl-2,3-dichloroalanine showed no depression.

The oxazolinone (XII) (0.267 g, i.e. 0.001 mole) was treated at 40° with a mixture of 0.2 g of acetic anhydride and 0.2 g of pyridine. The clear solution was set aside overnight, and on the next day a colorless crystalline precipitate appeared in the dark-red solution. The precipitate was filtered off and found to be unchanged oxazolinone (XII), m.p. 108-109°. All attempts at converting the oxazolinone (XII) into 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one (XVI) were unsuccessful. It was found also that the oxazolinone (XII) was unaffected when heated to 150°.

4-Acetoxy-4-(bromomethyl)-2-phenyl-2-oxazolin-5-one (XIII). A mixture of 2.7 g (0.01 mole) of N-benzoyl-3-bromo-2-hydroxyalanine and 5 ml of acetic anhydride was heated for five minutes at 70-80°. The solution was poured into ice water, and the precipitate that formed was repeatedly washed with bicarbonate solution, and was then washed with water and dried over phosphoric oxide in a vacuum desiccator. The product was 1.3 g (41%) of 4-acetoxy-4-(bromomethyl)-2-phenyl-2-oxazolin-5-one, which melted, after recrystallization from absolute alcohol, at 134-135°. A mixture test with a sample prepared from N-benzoyl-2,3-dibromoalanine showed no depression.

2-Benzyl-4-(bromomethylene)-2-oxazolin-5-one (XIV). 1) A mixture of 2.84 g (0.01 mole) of 3-bromo-2-hydroxy-N-(phenylacetyl)alanine (m.p. 105-106°) and 5 ml of acetic anhydride was heated for 15 minutes at 60-65°. The orange-yellow solution was cooled and poured into three times its volume of ice water. A semisolid precipitate formed, and it was separated, washed first with a saturated solution of sodium bicarbonate and then with water, and dried over phosphoric oxide in a vacuum desiccator. The product was 0.5 g (18.8%) of 2-benzyl-4-(bromomethylene) -2-oxazolin-5-one, melting at 101° with decomposition. After being purified as already described [1], it melted at 106-107°. A mixture test with a sample prepared from 2,3-dibromo-N-(phenylacetyl)alanine showed no depression.

Found %: C 49,35; H 3,28; Br 30,09
$C_{11}H_8O_2NBr$ Calculated %: C 49,62; H 3,00; Br 30,08

2) A mixture of 3.29 g (0.01mole) of 3-bromo-2-ethoxy-N-(phenylacetyl)alanine and 20 ml of acetic anhydride was heated for 30 minutes at 60-70°, and acetic anhydride was then removedunder reduced pressure until crystallization began. The crystalline precipitate was pasted with a small amount of absolute ether, and the residue was filtered off and washed with a little ether. The product was 1.5 g (56%) of the oxazolinone (XIV), melting with decomposition at 109-111°. A mixture test with a sample prepared from 2,3-dibromo-N-(phenylacetyl)alanine showed no depression.

4-Chloro-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one (XV). N-Benzoyl-2,3-dichloroalanine (2.62 g, i.e. 0.01 mole) was suspended in 20 ml of absolute benzene, and the mixture was boiled with 2.1 g (0.01 mole) of phosphorus pentachloride for two hours. The mixture was then evaporated to dryness under reduced pressure. The residue was dissolved in a little benzene, and petroleum ether was added. A resinous precipitate formed and was separated; solvent was removed in a vacuum. The product was 1.8 g of 4-chloro-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one (XV), m.p. 70-74°. It was not found possible to purify the oxazolinone (XV) by crystallization. It is readily soluble in benzene and ether, and moderately soluble in petroleum ether.

Found %: C 49,35; H 3,45
$C_{10}H_7O_2NCl_2$ Calculated %: C 49,18; H 2,86

This substance reacts with water and with methanol even at room temperature with formation of N-benzoyl-3-chloro-2-hydroxyalanine and the methyl ester of N-benzoyl-3-chloro-2-methoxyalanine respectively. These products showed no depression in mixture tests with samples prepared by other methods. The oxazolinone (XV) is not affected by long boiling in benzene (no elimination of HCl. occurs), and it is unaffected also when washed with a saturated solution of sodium bicarbonate.

2,2-Bis(benzamido)-3-chloropropionic Acid (XVII). 4-Acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one (0.6 g, i.e. 0.002 mole) was heated at 80° with a saturated solution of sodium bicarbonate. The solution was cooled and the precipitate present was filtered off (0.1 g of benzamide, giving no melting point depression in a mixture test with known benzamide). The filtrate was acidified to Congo Red with 25% sulfuric acid, and an oil was precipitated which gradually solidified. The precipitate was filtered off, washed with cold water, and dried over phosphoric oxide in a vacuum desiccator. The product was 0.15 g of 2,2-bis(benzamido)-3-chloropropionic acid (XVII), m.p. 140-141° (from dichloroethane).

Found %: C 58.86; H 4.29; N 7.78; Cl 9.87

$C_{17}H_{15}O_4N_2Cl$ Calculated %: C 58.87; H 4.33; N 8.01; Cl 10.24

The acid (XVII) is readily soluble in alcohol and benzene, and can be crystallized from hot water. When heated with acetic anhydride at 60-70°, it immediately gives benzonitrile and 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one (XVI), identical with the 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one prepared by another method. The acid mother liquor that remained after isolation of the acid (XVII) was treated with a 0.5% solution of 2,4-dinitrophenylhydrazine in 2 N HCl and 0.10 g of the 2,4-dinitrophenylhydrazone of (benzoyloxy)pyruvic acid was obtained. This melted at 168-171° (from alcohol) and was identical with the hydrazone obtained from (benzoyloxy)pyruvic acid.

SUMMARY

1. It has been shown that N-acyl-2,3-dihaloalanines readily exchange their 2-halogens for hydroxyl, alkoxyl, acetoxy, and other groups.

2. It has been shown that in the presence of acetic anhydride 3-halo-2-hydroxy-N-(phenylacetyl)alanines and 2-alkoxy-3-halo-N-(phenylacetyl)alanines are readily converted into 2-benzyl-4-(halomethylene)-2-oxazolin-5-ones.

3. When acetic anhydride acts upon N-benzoyl-3-chloro-2-hydroxyalanine, 4-acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one is formed; whereas when it acts on 2,2-bis(benzamido)-3-chloropropionic acid, the product is 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one.

Received April 9, 1954

N.D. Zelinsky Institute of Organic Chemistry of the USSR Academy of Sciences

LITERATURE CITED

[1] O.V. Kildisheva, L. P. Rasteikene, and I. L. Knunyants, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, No. 2, 260.*

---

* See Consultants Bureau Translation, p. 231.

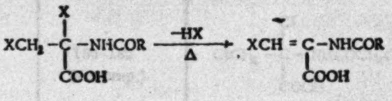
BLANK
PAGE

REACTIONS OF MERCAPTO AMINO ACIDS

COMMUNICATION 6. 2-(ACYLAMINO)-3-HALOACRYLIC ACIDS AND THEIR DERIVATIVES

O. V. Kildisheva, M. G. Linkova, and I. L. Knunyants

We have previously shown [1] that N-acyl-2,3-dihaloalanines are readily converted by the action of acetic anhydride into oxazolinones, having a side group that may be saturated or unsaturated depending on the identity of the N-acyl group. Further investigation of the properties of N-acyl-2,3-dihaloalanines has shown that, when they are heated in anhydrous solvents, hydrogen halide is readily eliminated and previously unknown 2-(acylamino)-3-haloacrylic acids (I, II, III, IV, in Table 1) are formed:

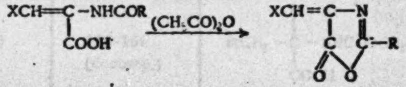


$$XCH_2-\underset{COOH}{\overset{X}{C}}-NHCOR \xrightarrow[\Delta]{-HX} XCH=\underset{COOH}{C}-NHCOR$$

X = Br, Cl; R = C_6H_5, $CH_2C_6H_5$

2-(Acylamino)-3-haloacrylic acids are stable compounds, which can be readily crystallized from various solvents in the form of colorless needles, can be reprecipitated with acid from aqueous solutions of their salts, and react normally with diazomethane with formation of the corresponding methyl 2-(acylamino)-3-haloacrylates.

When treated with dehydration agents, 2-(acylamino)-3-haloacrylic acids (with the exception of 2-(benzyloxycarbonyl amino)-3-bromoacrylic acid) are converted into 2-aryl(or aralkyl)-4-(halomethylene)-2-oxazolin-5-ones (Table 2):



(VI) X = Cl, R = $CH_2C_6H_5$; (VII) X = Br, R = $CH_2C_6H_5$;

(VIII) X = Cl, R = C_6H_5; (IX) X = Br, R = C_6H_5;

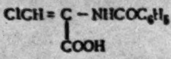
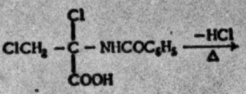
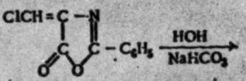
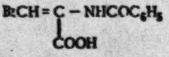
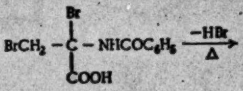
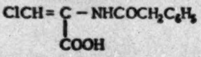
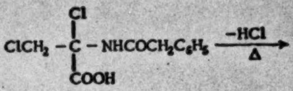
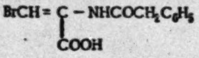
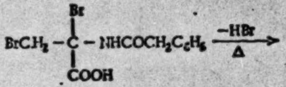
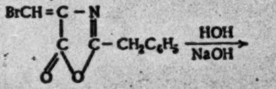
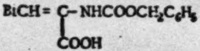
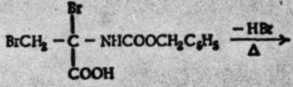
Oxazolinones (VI) and (VII), prepared from 3-chloro- and 3-bromo-2-(2-phenylacetamido)acrylic acids, were found to be identical with the oxazolinones prepared by the action of acetic anhydride on 2,3-dichloro- and 2,3-dibromo-N-(phenylacetyl)alanines respectively [1]. Again, the oxazolinone (VIII) was found to be identical with the 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one obtained previously be a method that left no doubt as to its structure, namely the action of thionyl chloride on 4-(hydroxymethylene)-2-phenyl-2-oxazolin-5-one [2]. The last compound was prepared by the action of acetic anhydride on an acetal of an (acylamino)malonaldehydic acid [3].

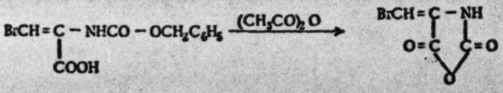
It is of interest that all of the synthesized 2-(acylamino)-3-haloacrylic acids give immediate intense colorations in presence of a carboxylic anhydride and pyridine or a pyridine base. For example, in presence of any anhydride (even an anhydride such as 2-benzyl-4-methyl-4-(2-phenylacetamido)-2-oxazolin-5-one) and a pyridine base, 3-bromo-2-(2-phenylacetamido)acrylic acid immediately gives a coloration, which is at first violet, but gradually becomes dark crimson.

Under the same conditions 2-benzamido-3-chloroacrylic acid gives a green coloration, which gradually changes to blue. These colors, which arise owing to the conversion of these acids into 2-aryl(or aralkyl)-4-(halomethylene-2-oxazolin-5-ones (which themselves give intense colorations with bases), enable 2-(acylamino)-3-haloacrylic acids to be used as sensitive reagents for the anhydride linkage.

When 2-(benzyloxycarbonylamino)-3-bromoacrylic acid is treated with acetic or trifluoroacetic anhydride, the internal anhydride of 3-bromo-2-(carboxyamino)acrylic acid (4-(bromomethylene)2,5-oxazolidinedione) (X) is formed; it melts with decomposition at 205-206° in a sealed capillary.

TABLE 1

2-(Acylamino)-3-haloacrylic acid		M.p.(°C)	Method of preparation	
 $\mathrm{ClCH{=}C(COOH){-}NHCOC_6H_5}$	(I)	160-161 (decomp.)	 $\mathrm{ClCH_2{-}C(Cl)(COOH){-}NHCOC_6H_5 \xrightarrow[\Delta]{-HCl}}$	(1)
				(2)
 $\mathrm{BrCH{=}C(COOH){-}NHCOC_6H_5}$	(II)	154-156 (decomp.)	 $\mathrm{BrCH_2{-}C(Br)(COOH){-}NHCOC_6H_5 \xrightarrow[\Delta]{-HBr}}$	
 $\mathrm{ClCH{=}C(COOH){-}NHCOCH_2C_6H_5}$	(III)	180-182 (decomp.)	 $\mathrm{ClCH_2{-}C(Cl)(COOH){-}NHCOCH_2C_6H_5 \xrightarrow[\Delta]{-HCl}}$	
 $\mathrm{BrCH{=}C(COOH){-}NHCOCH_2C_6H_5}$	(IV)	174-175 (decomp.)	 $\mathrm{BrCH_2{-}C(Br)(COOH){-}NHCOCH_2C_6H_5 \xrightarrow[\Delta]{-HBr}}$	(1)
				(2)
 $\mathrm{BrCH{=}C(COOH){-}NHCOOCH_2C_6H_5}$	(V)	163-164 (decomp.)	 $\mathrm{BrCH_2{-}C(Br)(COOH){-}NHCOOCH_2C_6H_5 \xrightarrow[\Delta]{-HBr}}$	

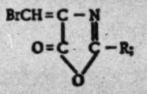


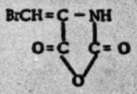
(X)

Other dehydrating agents, such as phosphorus pentachloride, have the same action.

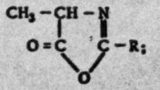
This internal anhydride is a representative of a new type of anhydride formed by unsaturated acylamino carboxylic acids.

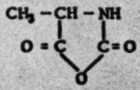
Series 1





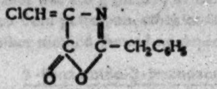
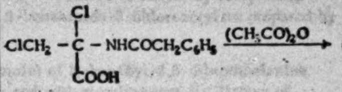
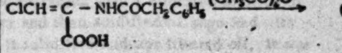
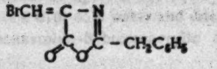
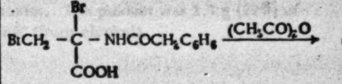
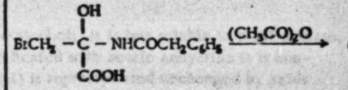
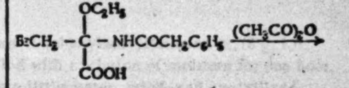
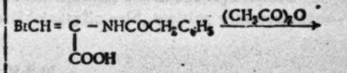
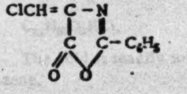
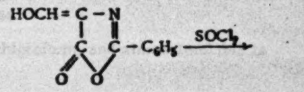
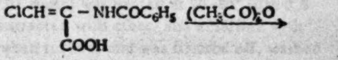
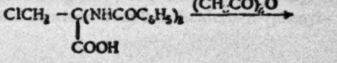
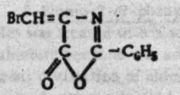
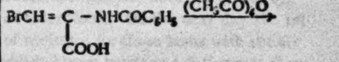
Series 2





A comparison of the properties of the derivatives of unsaturated acylamino carboxylic acids that we have synthesized (Series I) with those of the corresponding derivatives of saturated acylamino carboxylic acids (Series II) has shown that the compounds in the new series are incomparably more stable. The internal anhydride (X), for example, can be recrystallized unchanged from alcohols, whereas even at room temperature the internal anhydride of N-carboxyalanine is decarboxylated and converted into a macromolecular polypeptide [4, 5].

TABLE 2

2-Aryl(or Aralkyl)-4-(halomethylene)-2-oxazolin-5-one		M.p. (°C)	Method of preparation	
	(VI)	114-115 (decomp.)	 $ClCH_2-\underset{\underset{COOH}{\vert}}{\overset{\overset{Cl}{\vert}}{C}}-NHCOCH_2C_6H_5 \xrightarrow{(CH_3CO)_2O}$	(1)
			 $ClCH=\underset{\underset{COOH}{\vert}}{C}-NHCOCH_2C_6H_5 \xrightarrow{(CH_3CO)_2O}$	(2)
	(VII)	112-114 (decomp.)	 $BrCH_2-\underset{\underset{COOH}{\vert}}{\overset{\overset{Br}{\vert}}{C}}-NHCOCH_2C_6H_5 \xrightarrow{(CH_3CO)_2O}$	(1)
			 $BrCH_2-\underset{\underset{COOH}{\vert}}{\overset{\overset{OH}{\vert}}{C}}-NHCOCH_2C_6H_5 \xrightarrow{(CH_3CO)_2O}$	(2)
			 $BrCH_2-\underset{\underset{COOH}{\vert}}{\overset{\overset{OC_2H_5}{\vert}}{C}}-NHCOCH_2C_6H_5 \xrightarrow{(CH_3CO)_2O}$	(3)
			 $BrCH=\underset{\underset{COOH}{\vert}}{C}-NHCOCH_2C_6H_5 \xrightarrow{(CH_3CO)_2O}$	(4)
	(VIII)	135-137 (decomp.)		(1)
			 $ClCH=\underset{\underset{COOH}{\vert}}{C}-NHCOC_6H_5 \xrightarrow{(CH_3CO)_2O}$	(2)
			 $ClCH_2-\underset{\underset{COOH}{\vert}}{C}(NHCOC_6H_5)_2 \xrightarrow{(CH_3CO)_2O}$	(3)
	(IX)	137 melts again at 189-192 (decomp.)	 $BrCH=\underset{\underset{COOH}{\vert}}{C}-NHCOC_6H_5 \xrightarrow{(CH_3CO)_2O}$	(1)

EXPERIMENTAL

2-Benzamido-3-chloroacrylic Acid (I). A mixture of 2.6 g of N-benzoyl-2,3-dichloroalanine and 200 ml of absolute benzene was boiled for 40-50 minutes, and then cooled. The crystalline precipitate was filtered off, and then washed, first with a little dry benzene, and then with absolute ether. The product was 1.1 g (50%) of 2-benzamido-3-chloroacrylic acid, melting with decomposition at 160-161° (from absolute alcohol). In a mixture test with a sample of the acid prepared from 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one there was no depression.

2-Benzamido-3-chloroacrylic acid is readily crystallized from acetic anhydride. When heating with acetic anhydride is prolonged, ready cyclization occurs with formation of the known 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one, m.p. 135-137°. When it is heated in a moist solvent a by-product of the reaction is 2,2-bis(benzamido)-3-chloropropionic acid, m.p. 140-141° (from absolute alcohol), identical with the acid obtained by hydrolysis of 4-acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one [6].

Methyl 2-Benzamido-3-chloroacrylate. 2-Benzamido-3-chloroacrylic acid (2.2 g, i.e. 0.01 mole) was suspended in 25 ml of absolute ether and treated with an ethereal solution of diazomethane until nitrogen ceased to be evolved. The almost clear solution was filtered, and ether was evaporated until crystallization began. The product was 1.5 g (62.5%) of methyl 2-benzamido-3-chloroacrylate, m.p. 86-87°, raised to 93-94° by recrystallization from petroleum ether or 50% methanol. A mixture test with methyl 2-benzamido-3-chloroacrylate prepared by another method showed no depression.

2-Benzamido-3-bromoacrylic Acid (II). A mixture of 10 g (0.03 mole) of N-benzoyl-2,3-dibromoalanine and 500 ml of benzene was boiled for two hours with exclusion of moisture and with simultaneous distillation of benzene and hydrogen bromide. The reddish-brown solution was cooled and extracted with a saturated solution of sodium bicarbonate. The alkaline solution was extracted with a little ether and then acidified to Congo Red with concentrated hydrochloric acid. An oil separated, and after a few minutes it solidified and was filtered off. It was washed with cold water and dried over phosphoric oxide in a vacuum desiccator. The product was 1.7 g (22%) of 2-benzamido-3-bromoacrylic acid, melting with decomposition at 155-156° (from alcohol).

Found %: C 44.10; H 3.16; Br 29.22

$C_{10}H_8O_3NBr$. Calculated %: C 44.28; H 2.95; Br 29.5

2-Benzamido-3-bromoacrylic acid is readily soluble in acetone and alcohol; it is less soluble in ethyl acetate, and almost insoluble in benzene, ether, and cold acetic anhydride. When heated with acetic anhydride it is converted into 4-(bromomethylene)-2-phenyl-2-oxazolin-5-one. The acid (II) is reprecipitated unchanged by acids from the aqueous solutions of its salts.

3-Chloro-2-(2-phenylacetamido)acrylic Acid (III). 1) 2,3-Dichloro-N-(phenylacetyl)alanine (2.76 g, i.e. 0.01 mole) was suspended in 200 ml of benzene, and the mixture was boiled with exclusion of moisture for one hour. The mixture was cooled and the precipitate was filtered off, washed with a little water, dried, and crystallized from alcohol. The product was 1.2 g (50%) of 3-chloro-2-(2-phenylacetamido)acrylic acid, melting with decomposition at 180-182°.

Found %: C 54.44; H 4.25; Cl 15.0; N 5.91

$C_{11}H_{10}O_3NCl$. Calculated %: C 55.11; H 4.2; Cl 14.8; N 5.84

The acid is readily soluble in alcohol and ethyl acetate, less soluble in chloroform, and almost insoluble in benzene.

2) 2-Benzyl-4-(chloromethylene)-2-oxazolin-5-one (2.21 g, i.e. 0.01 mole) was heated at 50-60° with 0.5 N NaOH until the oxazolinone dissolved. The clear solution was cooled, extracted with ether, and acidified with concentrated hydrochloric acid. An oily precipitate formed. It solidified when rubbed, and was filtered off, washed with water, dried, and recrystallized from absolute alcohol. The product was 0.99 g (40%) of 3-chloro-2-(2-phenylacetamido)acrylic acid, m.p. 180-181°, undepressed by admixture of the acid obtained from 2,3-dichloro-N-(phenylacetyl)alanine.

3-Bromo-2-(2-phenylacetamido)acrylic Acid (IV). 1) 2-(2-Phenylacetamido)acrylic acid (20 g, i.e. 0.1 mole) was treated with a solution of 16 g (0.1 mole) of bromine in 160 ml of chloroform. On the next day 200 ml of absolute benzene was added, and the mixture was boiled with exclusion of moisture for three hours with simultaneous distillation of chloroform, benzene, and hydrogen bromide. The reddish-brown benzene solution was then extracted with a saturated solution of sodium bicarbonate, the alkaline solution was separated from the benzene, and residual benzene was removed by extraction with a little ether. The solution was acidified to Congo Red with concentrated hydrochloric acid, and the precipitate that formed was filtered off, washed with water, and dried over phosphoric oxide in a vacuum desiccator. The product was 20.5 g (72%) of 3-bromo-2-(2-phenylacetamido) acrylic acid melting with decomposition at 174-175° after recrystallization from absolute alcohol.

Found %: C 46.88; H 3.63; N 5.21

$C_{11}H_{10}O_3NBr$. Calculated %: C 46.47; H 3.52; N 4.93

3-Bromo-2-(2-phenylacetamido)acrylic acid is readily soluble in alcohol, acetone, and ethyl acetate; it has limited solubility in ether; and it is almost insoluble in water. It is reprecipitated unchanged by acids from aqueous solutions of its salts. It was found that an alkaline solution of 3-bromo-2-(2-phenylacetamido)acrylic acid did not give a violet color with ferric chloride, but after being warmed with 2 N NaOH for five minutes, ferric chloride gave the reddish-violet color characteristic for hydroxypyruvic acid. When the alkaline solution was acidified, 3-bromo-2-(2-phenylacetamido)acrylic acid was precipitated in almost quantitative yield. More prolonged heating (15 minutes) with 2 N NaOH resulted in decomposition, and 2-phenylacetamide was found among the decomposition products; it melted at 155-156°, and there was no depression in admixture with known 2-phenylacetamide.

2) 2-Benzyl-4-(bromomethylene)-2-oxazolin-5-one (11.8 g, i.e. 0.44 mole) was suspended in 200 ml of 0.5 N NaOH and heated at 70-80° until solution was complete (15 minutes). The solution was cooled, filtered, and acidified to Congo Red with concentrated hydrochloric acid. The precipitate was filtered off, washed with a little water, and dried over phosphoric oxide in a vacuum desiccator. The product was 4 g (32.5%) of 3-bromo-2-(2-phenylacetamido)acrylic acid, m.p. 172-173° (from acetone or alcohol), undepressed by admixture of a sample prepared from 2,3-dibromo-N-(phenylacetyl)alanine.

2-(Benzyloxycarbonylamino)-3-bromoacrylic Acid (V). N-(Benzyloxycarbonyl)-2,3-dibromoalanine (11 g, i.e. 0.05 mole) was treated with a solution of 8 g (0.05 mole) of bromine in 80 ml of chloroform. After one hour, the chloroform solution was evaporated to one-half of its original volume, 300 ml of absolute benzene was added, and the mixture was boiled with exclusion of moisture for four hours. It was then cooled, and the acid was isolated in the manner described for the acid (IV). The precipitate was filtered off, washed several times with cold water, and dried over phosphoric oxide in a vacuum desiccator. The product was 8.2 g (60%) of 2-(benzyloxycarbonylamino)-3-bromoacrylic acid, melting with decomposition at 163-164° (from aqueous alcohol).

2-(Benzyloxycarbonylamino)-3-bromoacrylic acid crystallizes in the form of colorless needles. It has limited solubility in benzene, ether, and chloroform, but is readily soluble in ethyl acetate and alcohol. It can be kept several months without change.

Found %: C 44.39; H 3.36; N 4.53

$C_{11}H_{10}O_4NBr$. Calculated %: C 44.0; H 3.33; N 4.66

Methyl 3-Bromo-2-(2-phenylacetamido)acrylate. 3-Bromo-2-(2-phenylacetamido)acrylic acid (5.68 g, i.e. 0.02 mole) was suspended in absolute ether and treated with an ethereal solution of diazomethane until evolution of nitrogen ceased. The whole of the acid went into solution. The solution was filtered rapidly and set aside at room temperature. After 10-15 minutes a crystalline precipitate began to form. The precipitate was filtered off and washed with a little ether. The product was 3.9 g (65%) of methyl 3-bromo-2-(2-phenylacetamido)acrylate, m.p. 90-91°. After recrystallization from absolute ether it melted at 100-101°.

Found %: C 48.19; H 4.07; N 4.85

$C_{12}H_{12}O_4NBr$. Calculated %: C 48.32; H 4.02; N 4.7

2-Benzyl-4-(chloromethylene)-2-oxazolin-5-one (VI). A mixture of 0.239 g (0.001 mole) of 3-chloro-2-(2-phenylacetamido)acrylic acid and 2 ml of acetic anhydride was heated at 80° for 15 minutes. The yellow solution was cooled and poured into ice water. The oil that was then precipitated solidified when rubbed. It was filtered off, washed with a saturated solution of sodium bicarbonate, dried, and recrystallized from ether. The product was 0.13 g (60%) of 2-benzyl-4-(chloromethylene)-2-oxazolin-5-one, melting with decomposition at 114-115°. In a mixture test with the oxazolinone prepared from 2,3-dichloro-N-(phenylacetyl)alanine there was no depression. With pyridine or a pyridine base the oxazolinone gave a characteristic dark-violet coloration.

2-Benzyl-4-(bromoethylene)-2-oxazolin-5-one (VII). A mixture of 2.8 g (0.01 mole) of 3-bromo-2-(2-phenylacetamido)acrylic acid and 10 ml of acetic anhydride was heated at 50-60° for 20 minutes. The acetic anhydride was distilled off at a residual pressure of 7 mm, and the residue was extracted with ether. The product was 2-benzyl-4-(bromomethylene)-2-oxazolin-5-one, m.p. 110-112°, undepressed by admixture of a sample prepared from 2,3-dibromo-N-(phenylacetyl)alanine.

4-(Chloromethylene)-2-phenyl-2-oxazolin-5-one (VIII). A mixture of 1.1 g (0.005 mole) of 2-benzamido-3-chloroacrylic acid and 10 ml of acetic anhydride was heated at 100° for 15 minutes. Acetic anhydride was then distilled off under reduced pressure until crystallization began. The crystalline precipitate was filtered off, washed first with a little ether and then with absolute alcohol, and dried over phosphoric oxide in a vacuum desiccator. The product was 0.82 g (80%) of 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one, m.p. 135-137° (from acetic anhydride), undepressed by admixture of a sample of the oxazolinone obtained from 4-(hydroxymethylene)-2-phenyl-2-oxazolin-5-one [2].

4-(Bromomethylene)-2-phenyl-2-oxazolin-5-one (IX). A mixture of 0.6 g (0.002 mole) of 2-benzamido-3-bromoacrylic acid (m.p. 155-156°) and 2 ml of acetic anhydride was heated at 90-100° for five minutes. The mixture was then cooled and poured into ten times its volume of ice water. The yellow crystalline precipitate was filtered off, carefully washed with water, and dried over phosphoric oxide in a vacuum desiccator. The product was 0.3 g (53%) of 4-(bromomethylene)-2-phenyl-2-oxazolin-5-one, melting first at 137°, then resolidifying, and then melting again with decomposition at 189-192° (from a mixture of alcohol and chloroform).

Found %: C 47.45; H 2.61; Br 31.42

$C_{10}H_6O_2NBr$. Calculated %: C 47.6; H 2.38; Br 31.7

4-(Bromomethylene)-2-phenyl-2-oxazolin-5-one is very soluble in chloroform and ether, of limited solubility in alcohol, and may be crystallized from acetic anhydride. It gives a dark-green color with pyridine. With an ethereal solution of aniline an ethereal solution of 4-(bromomethylene)-2-phenyl-2-oxazolin-5-one gives 4-(anilinomethylene)-2-phenyl-2-oxazolin-5-one, m.p. 153-155° (from alcohol), undepressed by admixture of a sample of 4-(anilinomethylene)-2-phenyl-2-oxazolin-5-one prepared from known 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one (152-155°).

Internal Anhydride of 3-Bromo-2-(carboxyamino)acrylic Acid (4-(Bromomethylene)-2,5-oxazolidinedione) (X). 2-(Benzyloxycarbonylamino)-3-bromoacrylic acid (3 g, i.e. 0.01 mole) was carefully mixed with 2.08 g (0.01 mole) of phosphorus pentachloride without permitting access of moisture. Reaction occurred with evolution of heat and vigorous evolution of hydrogen chloride. After 5-10 minutes the reaction mixture was diluted with a little absolute ether and filtered. The residue on the filter was washed with petroleum ether. An almost quantitative yield was obtained of the internal anhydride of 3-bromo-2-(carboxyamino)acrylic acid, melting with decomposition at 198-200° in a sealed capillary. The anhydride is readily soluble in ether, alcohol, and dioxan. When recrystallized from alcohol (dissolution temperature not above 55°), there are great losses; the recrystallized product melts with decomposition at 205-206° in a sealed capillary.

Found %: C 25.26; H 1.19; N 7.51; Br 41.62
$C_4H_2O_3NBr$. Calculated %: C 25.0; H 1.04; N 7.24; Br 41.6.

SUMMARY

1. It has been shown that 2-(acylamino)-3-haloacrylic acids can be prepared by the thermal elimination of hydrogen halide from N-acyl-2,3-dihaloalanines.

2. It has been shown that, by the action of acetic anhydride, 2-(acylamino)-3-haloacrylic acids are converted into 2-aryl(or aralkyl)-4-(halomethylene)-2-oxazolin-5-ones.

3. By the action of dehydrating agents on 2-(benzyloxycarbonylamino)-3-bromoacrylic acid, the first representative of the class of unsaturated internal anhydrides of carboxyamino acids has been prepared, namely the internal anhydride of 3-bromo-2-(carboxyamino)acrylic acid.

Recieved April 9, 1954

N. D. Zelinsky Institute of Organic Chemistry of
the USSR Academy of Sciences

LITERATURE CITED

[1] O. V. Kildisheva, L. P. Rasteikene, and I. L. Knunyants. Bull. Acad. Sci. USSR Div. Chem. Sci., 1955. No. 2, 260.*

[2] Chemistry of Penicillin. Princeton, N. J., 1949, p. 823.

[3] Chemistry of Penicillin. Princeton, N. J., 1949, p. 523.

[4] C. Asbury et al., Nature 162, 569 (1948).

[5] R. Woodward, C. Schramm, J. Am. Chem. Soc. 69, 1551 (1947).

[6] O. V. Kildisheva, M. G. Linkova, and I. L. Knunyants. Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, No. 2, 271.**

---

* See Consultants Bureau Translation, p. 231.

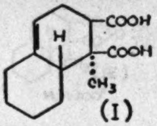
** See Consultants Bureau Translation, p. 241.

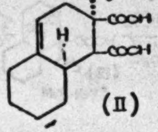
STEREOCHEMISTRY OF CYCLIC COMPOUNDS

COMMUNICATION 6. LACTONIZATION OF cis- AND trans-1,2,3,5,6,7,8,8a-OCTAHYDRO-1,2-NAPHTHALENEDICARBOXYLIC ACIDS

I. N. Nazarov, V. F. Kucherov, and V. M. Andreev

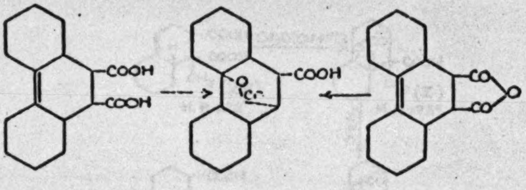
In the course of a study of the displacement of double bonds in the isomeric cis-1,2,3,5,6,7,8,8a-octahydromethyl-1,2-naphthalenedicarboxylic acids (I) and (II) under acid conditions [1], we have made some interesting observations concerning their lactonization.


(I)

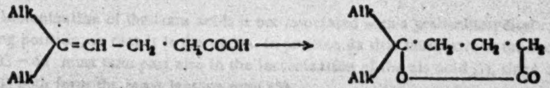

(II)

We have found that, when these acids are heated with a mixture of acetic acid and hydrogen chloride, they both give crystalline substances of the same composition $C_{13}H_{18}O_4$. These crystalline substances do not contain a double bond and have only one free carboxyl group: they do not decolorize a chloroform solution of bromine, they are not hydrogenated in acetic acid in presence of platinum oxide, they behave as monocarboxylic acids when titrated, and they give monoesters of composition $C_{14}H_{20}O_4$ with an ethereal solution of diazomethane. All of these facts indicate that, when the unsaturated cis-dicarboxylic acids (I) and (II) are treated with a mixture of acetic acid and hydrogen chloride, lactonization occurs with participation of one of the carboxyls and the double bond in the ring with formation of the corresponding saturated monocarboxylic lactone acids.

This tendency for unsaturated cyclic carboxylic acids to undergo lactonization has been noted several times before [2]. It has been examined in some detail by Adams and Gruber for the adduct obtained by the condensation of bicyclohexenyl with maleic anhydride [3]. They showed that this dibasic acid and its anhydride are readily cyclized by treatment with an alcoholic solution of hydrogen chloride with formation of a lactone acid or its ester:



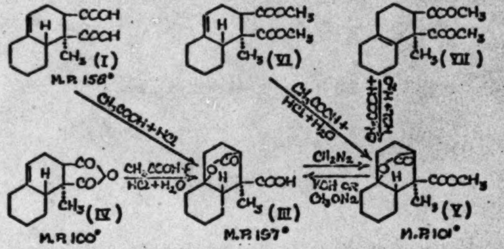
The authors ascribed a δ-lactone structure to the lactone acid, basing their view on the regularities previously found in a study of the lactonization of γ,δ-unsaturated fatty acids [4]. It was shown that, when these acids have alkyl groups on the δ-carbon, exclusive formation of δ-lactones occurs:



$$(Alk)_2C{=}CH-CH_2\cdot CH_2COOH \longrightarrow (Alk)_2\overset{}{C}\cdot CH_2\cdot CH_2\cdot CH_2 \quad (O{-}CO)$$

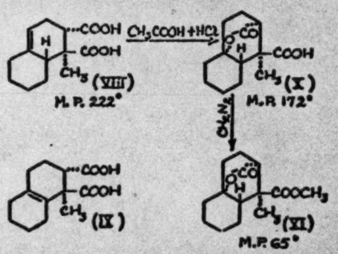
For the condensation of allylcyclohexanol with maleic anhydride, it has been inferred that the adduct is a δ-lactone from an examination of molecular models [5]. The tendency for γ, δ-unsaturated acids substituted on the δ-carbon to give δ-lactones has been recently applied in the synthesis of ambreinolide [6]. The structural peculiarities of the unsaturated bicyclic cis-dicarboxylic acids (I) and (II) that we have selected for study have enabled us to investigate their lactonization in detail, to prove the structures of the lactones formed, and to investigate some of their reactions.

When the cis acid (I) was heated with acetic acid saturated with dry hydrogen chloride, the cis lactone acid (III), m.p. 197°, was readily formed in high yield. It was obtained also from the corresponding cis anhydride (IV). The cis lactone acid (III) behaved as a monocarboxylic acid in titration, and it was found that it does not contain a double bond. With diazomethane it gave the cis lactone ester (V), m.p. 101°. It was found that the lactone ester (V) can be obtained also by the partial hydrolysis in an acid medium of the cis diester (VI) or of the isomeric cis diester (VII), which has a double bond between the rings. These facts show that the lactone ring is always formed with the participation of the same carbon atom of the ring and the same carboxyl group.



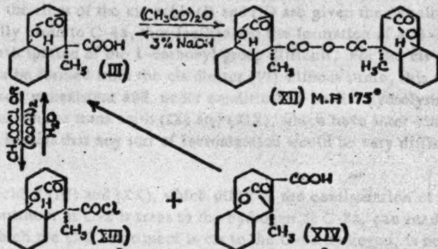
The fact that the cis lactone ester (V) is not isomerized by treatment with sodium methoxide, but is only saponified with formation of the original cis lactone acid (III) in good yield, shows that it is the secondary carboxyl group at C-2 that takes part in lactone formation. The formation of the cis lactone ester (V) from the cis diesters (VI) and (VII) also provides confirmation of this conclusion, since it is known that an esterified secondary carboxyl is more readily hydrolyzed than a tertiary ester grouping.

In order to resolve the questions of which carbon atom of the ring (C-4a or C-8a) takes part in the lactonization and whether or not lactonization is accompanied by displacement of the double bond to the inter-ring position, we have studied the lactonization of the isomeric trans acids (VIII) and (IX). It was found that, under lactonization conditions, the trans acid (VIII) readily gives the translactone acid (X), m.p. 172°, in good yield, and this is converted by diazomethane into the trans. lactone ester (XI), m.p. 65°. On the other hand, the trans acid (IX), which has an inter-ring double bond, was found to be quite incapable of lactonization, and when it was heated with acetic acid and hydrogen chloride, it was recovered unchanged.



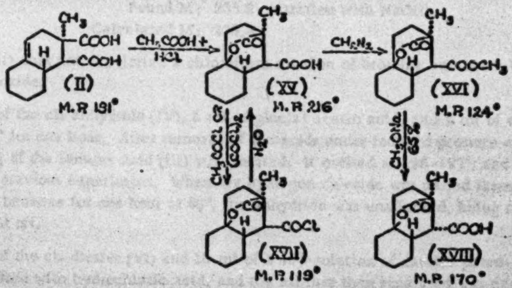
These results show that the lactonization of the trans acids is not associated with a preliminary displacement of the double bond to the inter-ring position, so that it is the carbon in position 4a that takes part in the lactonization. Moreover, the same carbon atom C-4a must take part also in the lactonization of the cis acid (I), since only then could the cis diesters (VI) and (VII) both form the same lactone ester (V).

We have studied some of the chemical reactions of the cis lactone acid (III), and they show that the lactone ring is very stable in this compound. For example, when the cis lactone acid (III) is boiled with acetic anhydride, it gives the anhydride (XII), m.p. 175°, the structure of which was proved by analysis and by determination of its molecular weight. Hydrolysis of this anhydride with weak alkali readily gives the original cis lactone acid (III). The reaction with acetyl chloride is more complex. From the mixture of the products of this reaction we have isolated two crystalline substances by fractional crystallization. One of these, m.p. 140°, corresponded in analysis to the acid chloride (XIII), and on hydrolysis with water it gave the original cis lactone acid (III) in quantitative yield. The same acid chloride (XIII) can be obtained in quantitative yield by the action of oxalyl chloride on the cis lactone acid (III), which provides final confirmation of its structure. The second crystalline product, m.p. 77°, corresponded by titration and analysis to an isomeric lactone acid $C_{13}H_{18}O_4$, and on standing it was gradually converted into the original cis lactone acid (III). This conversion goes to completion in presence of a little hydrogen chloride. It is possible that the lactone acid of m.p. 77° is the γ-lactone acid (XIV). Owing to the inaccessibility of this lactone acid, we were unable to investigate it in greater detail.

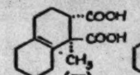


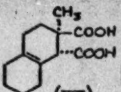
A study was made also of transformations of the cis acid (II) corresponding to those described above for the cis acid (I). When the cis acid (II) was heated with a mixture of acetic acid and hydrogen chloride, the stable cis lactone acid (XV), m.p. 216°, was readily formed in good yield. With diazomethane the lactone acid yielded the corresponding cis lactone ester (XVI), m.p. 124°, and with acetyl or oxalyl chloride it gave a good yield of the acid chloride (XVII), which could be hydrolyzed to the original cis lactone acid (XV). No by-products were isolated in this reaction.

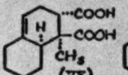
In view of its δ-lactone structure, the cis lactone acid (XV) should be capable of undergoing isomerization when treated with sodium methoxide, and this is what is actually observed. It was found that the cis lactone ester (XVI), unlike the cis lactone ester (V), yielded a new lactone acid of m.p. 170° when isomerized with sodium methoxide. This substance, in accordance with its method of preparation, should be the trans lactone acid (XVIII).

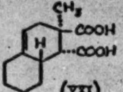


Like the trans acid (IX), the trans acid (XIX) with an inter-ring double bond is not able to form lactones. The isomeric trans acids (XX) and (XXI) are also unable to give lactones, and they are peculiar also in being unable to undergo isomerization with displacement of the double bond to the inter-ring position [7].


(IX)


(XIX)


(XX)


(XXI)

The steric hindrances to the lactonization of the isomeric acids (IX), (XIX), (XX), and (XXI) may be in some measure explained with the aid of molecular models.

Molecular models in which the rings of the cis acids (I) and (II) are given the "chair" conformation indicate that the carboxyl at C-2 is spatially close to C-4a, thus facilitating the formation of a δ-lactone and making the formation of a γ-lactone with participation of the 1-carboxyl group difficult. For the cis diester (VII) with the double bond between the rings, which can be formed from the cis diester (VI) without strain, this approach is so close that the cis acid corresponding to it is almost nonexistent and, under conditions of partial hydrolysis, lactonization to the cis lactone ester (V) is bound to occur. In the trans acids (IX) and (XIX), which have inter-ring double bonds, the spatial disposition of the carboxyl groups is such that any sort of lactonization would be very difficult, and in fact no lactonization occurs.

Of the two erpmeric trans acids (VIII) and (XX), which differ in the configuration of the hydrogen at C-8a, the trans acid (VIII), in which the substituent at C-2 is trans to the hydrogen at C-8a, can readily give a δ-lactone, whereas the trans acid (XX), in which the C-2 substituent is cis to the C-8a hydrogen, is not able to lactonize. This inference, which is in accord with the experimental results, is a further confirmation of the configurations that have been assigned to these acids [7] and to the trans acid (XXI), the spatial configuration of which should hinder lactonization. The molecular models show also that a displacement of the double bond into the inter-ring position will be extremely difficult in the trans acids (XX) and (XXI) and can be effected only by a complete rearrangement of the whole spatial configuration of the molecule.

EXPERIMENTAL

Lactonization of cis-1,2,3,5,6,7,8,8a-Octahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (I)

a) A mixture of 10 g of the cis acid (I) and 100 ml of glacial acetic acid saturated with hydrogen chloride was heated for 90 minutes at 60°. The residue after removal of acetic acid under reduced pressure was a crystalline substance of m.p. 192-193.5°. Crystallization from a large volume of water yielded 8.2 g of the pure cis lactone acid (III) in the form of long glistening needles, m.p. 197-197.5°.

Found %: C 65.29; 65.23; H 7.81; 7.50
$C_{13}H_{18}O_4$. Calculated %: C 65.52; H 7.53

Found M: 235.2; (titration with NaOH)
$C_{13}H_{18}O_4$. Calculated M: 238.3

The cis lactone acid (III) does not decolorize a chloroform solution of bromine and is not hydrogenated in acetic acid in presence of platinum oxide.

b) A mixture of 0.5 g of the cis anhydride (IV), 5 ml of glacial acetic acid, and 1 ml of concentrated hydrochloric acid was heated at 60° for one hour. After removal of the acids under reduced pressure and crystallization of the residue from water, 0.25 g of the lactone acid (III) was isolated; it melted at 196-197°, and was identical with the substance obtained in the previous experiment. When dry hydrogen chloride was passed through a solution of the cis anhydride (IV) in absolute benzene for one hour at 60°, the anhydride was unaffected, being recovered unchanged when the benzene was distilled off.

c) A mixture of 0.8 g of the cis diester (VI) and 10 ml of a 40% solution of caustic potash was boiled for four hours. The mixture was acidified with hydrochloric acid, and the oil that then separated was extracted with ether. The ether was distilled off, and the liquid residue was boiled with 6 ml of 5% hydrochloric acid until solution was complete. When the solution was cooled, 0.4 g of a crystalline substance of m.p. 190-192°, separated. Two recrystallizations from water yielded 0.3 g of the cis lactone acid (III), m.p. 196-197°, identical with that prepared in the preceding experiments.

The cis Lactone Ester (V)

a) A suspension of 3.1 g of the cis lactone acid (III) in ether was treated with an excess of an ethereal solution of diazomethane. After removal of ether, 3.2 g of crystals melting at 89-91° was obtained. Crystallization from a small amount of absolute ether yielded 2.8 g of pure cis lactone ester (V), m.p. 100-101°.

	Found %:	C 66.75; 66.84;	H 8.10; 8.07
$C_{14}H_{20}O_4$.	Calculated %:	C 66.65;	H 7.99

When the cis lactone ester (V) was hydrolyzed at the boil with 40% caustic potash, a good yield was obtained of the original cis lactone acid (III), m.p. 195-197° after recrystallization from water.

b) A solution prepared by dissolving 0.5 g of the cis diester (VI) in a mixture of 5 ml of glacial acetic acid and 1 ml of concentrated hydrochloric acid was set aside at room temperature overnight. The solvents were distilled off under reduced pressure, leaving a liquid residue, which crystallized when petroleum ether was added. Crystallization from ether yielded 0.35 g of pure cis lactone ester (V), m.p. 99-100°, identical with the substance obtained in the preceding experiment.

c) A mixture of 1.0 g of the cis diester (VII), 5 ml of glacial acetic acid, and 1 ml of concentrated hydrochloric acid was heated at 60° for two hours. The liquid residue remaining after removal of solvents at reduced pressure crystallized when treated with petroleum ether. The product was 0.45 g of crystals, melting at 94-96°. After crystallization from ether the melting point was 100-101°, undepressed by admixture of some of the cis lactone ester (V) obtained in the preceding experiment.

Attempt to Isomerize the cis Lactone Ester (V)

To a solution of 5 g of sodium in 125 ml of absolute methanol, 1.9 g of the cis lactone ester (V) was added, and the mixture was boiled for twelve hours. After removal of methanol under reduced pressure, the residue was dissolved in water, and the resulting solution was evaporated down in a porcelain dish on a water bath. The residue of salts was dissolved in the least possible amount of water, and the solution was acidified with hydrochloric acid. The oil that separated gradually solidified. The product (1.55 g) had a wide melting range (125-160°). Two crystallizations from ether yielded 0.85 g of a substance melting at 195-197°, which was found to be identical with the cis lactone acid (III). No other individual reaction products could be isolated.

Action of Acetic Anhydride on the cis Lactone Acid (III)

A mixture of 2.0 g of the cis lactone acid (III), m.p. 197-197.5°, and 20 ml of acetic anhydride was boiled for one hour. After removal of acetic anhydride under reduced pressure, a liquid reaction product was obtained, and this solidified when treated with benzene and petroleum ether. Crystallization from a mixture of benzene and petroleum ether yielded 1.2 g of a crystalline substance melting at 160-164°. After being recrystallized twice from a mixture of benzene and petroleum ether, the substance had a constant melting point of 174-175° and corresponded in analysis to the anhydride (XII).

	Found %:	C 68.32; 68.07;	H 7.44; 7.58
$C_{26}H_{34}O_7$.	Calculated %:	C 68.10;	H 7.48;
	Found M:	445.4 (cryoscopically in benzene)	
$C_{26}H_{34}O_7$.	Calculated M:	458.5	

A short boil with 3% caustic soda hydrolyzed the anhydride (XII) quantitatively to a substance of m.p. 195-196°, which was found to be identical with the cis lactone acid (III).

Action of Acetyl Chloride on the cis Lactone Acid (III)

The cis lactone acid (III) (1.5 g) was boiled with acetyl chloride (15 ml) for one hour. The cyrstalline reaction product obtained after removal of acetyl chloride was washed on the filter with a small amount of petroleum ether to which a few drops of diethyl ether had been added. The crystals obtained (1.2 g) melted at 109-121°, and when these were crystallized from ether, 0.6 g of a pure substance melting at 139-140° was obtained (fine glistening needles). This substance contained chlorine and corresponded in analysis to the acid chloride (XIII) of the cis lactone acid (III). The original cis lactone acid (III) was recovered quantitatively when this acid chloride was boiled with water.

	Found %:	C 61.36; 61.20;	H 7.03; 6.82;	Cl 13.77; 13.59
$C_{13}H_{17}O_3Cl$.	Calculated %:	C 60.81;	H 6.68;	Cl 13.81

The solution obtained by washing the crude reaction product was evaporated to low bulk, when 160 mg of crystals melting at 75.5-76.5° separated. After recrystallization from ether the substance melted at 76.5-77°, was free from chlorine, and corresponded by titration and elementary analysis to the isomeric cis lactone acid (XIV).

Found %: C 65.25; 65.30; H 7.26; 7.37
$C_{13}H_{18}O_4$. Calculated %: C 65.52; H 7.53

Found M: 231.8 (titration with NaOH)
$C_{13}H_{18}O_4$. Calculated M: 238.3

When kept, the cis lactone acid (XIV) was gradually converted into the cis lactone acid (III). This change occurred particularly readily when a little hydrogen chloride was present. Owing to its inaccessibility and instability, we were not able to make a more detailed study of the chemical properties of the cis lactone acid (XIV).

Acid Chloride (XIII) of the cis Lactone Acid (III)

Oxalyl chloride (0.5 ml) was added to a solution of 0.5 g of the cis lactone acid (III) in 5 ml of absolute benzene, and the mixture was heated at 50° for 2 hours 30 minutes. The residue remaining after removal of solvent crystallized when treated with petroleum ether. The product was 0.5 g of a substance melting at 138-139°. After recrystallization from ether it melted at 139-140°, and there was no depression in a mixture test with the acid chloride (XIII) prepared previously by the action of acetyl chloride on the cis lactone acid (III).

Lactonization of cis-1,2,3,5,6,7,8,8a-Octahydro-2-methyl-1,2-naphthalenedicarboxylic Acid (II)

A mixture of 1.0 g of the cis acid (II), m.p. 180-181°, and 10 ml of glacial acetic acid saturated with dry hydrogen chloride was heated at 60° for one hour. The acetic acid was driven off under reduced pressure, and, after crystallization from a small amount of water, the crystalline residue yielded 0.75 g of pure cis lactone acid (XV) in the form of fine needles melting at 216-216.5°.

Found %: C 65.74; 65.40; H 7.58; 7.69
$C_{13}H_{18}O_4$. Calculated %: C 65.52; H 7.53

Found M: 230.9 (titration with NaOH)
$C_{13}H_{18}O_4$. Calculated M: 238.3

The cis Lactone Ester (XVI)

The cis lactone acid (XV) of m.p. 215-216° (0.5 g) was treated in ether suspension with an excess of ethereal diazomethane. After removal of ether and treatment of the residue with petroleum ether, 0.45 g of the cis lactone ester (XVI), m.p. 119-121°, was obtained. After crystallization from ether it had a constant melting point of 123-124°.

Found %: C 66.87; 66.85; H 7.91; 8.01
$C_{14}H_{20}O_4$. Calculated %: C 66.65; H 7.99

When the cis lactone ester (XVI) was hydrolyzed with boiling 30% caustic potash, the original cis lactone acid (XV), m.p. 214-216°, was obtained in good yield.

Acid Chloride (XVII) of the cis Lactone Acid (XV)

A solution of 0.15 g of the cis lactone acid (XV) and 0.5 ml of oxalyl chloride in 2 ml of absolute benzene was heated at 50° for two hours. After removal of solvent, 170 mg of crystals melting at 118-120° were obtained, and recrystallization of these from ether yielded the pure acid chloride (XVII), m.p. 118-119°.

Found %: C 60.68; 60.66; H 6.63; 6.69; Cl 13.88; 13.90
$C_{13}H_{17}O_3Cl$. Calculated %: C 60.81; H 6.68; Cl 13.81

The same acid chloride (XVII) was the main product when the reaction was carried out with acetyl chloride. Hydrolysis of the acid chloride (XVII) with water gave a quantitative yield of the original cis lactone acid (XV).

The trans Lactone Acid (XVIII)

The cis lactone ester (XVI) of m.p. 123-124° (0.47 g) was added to a solution of 1.2 g of sodium in 35 ml of absolute methanol, and the mixture was boiled for 15 hours. The methanol was distilled off, 10 ml of water was added, and the solution was boiled for a further five hours. The mixture was evaporated in a porcelain dish, and the precipitate of salts was filtered off and dissolved in water. The solid obtained by acidification of this solution was crystallized twice from benzene, and 0.25 g of the trans lactone acid (XVIII), m.p. 169-170°, was obtained.

Found %: C 65.49; 65.59; H 7.67; 7.54

$C_{13}H_{18}O_4$. Calculated %: C 65.52; H 7.53

Found M: 232.1 (titration with NaOH)

$C_{13}H_{18}O_4$. Calculated M: 238.3

Lactonization of trans-1,2,3,5,6,7,8,8a-Octahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (VIII)

The trans acid (VIII) of m.p. 221-222° (1.0 g) was heated at 40° for one hour with 10 ml of a saturated solution of dry hydrogen chloride in glacial acetic acid. Acetic acid was distilled off under reduced pressure, and the semisolid residue solidified when treated first with benzene and then with ether, these solvents being added to the residue and then removed by distillation. The product was washed on the filter with a mixture of two parts of petroleum ether and one of diethyl ether, and 0.82 g of a substance of m.p. 163-166° was obtained. After crystallization from a large volume of water the pure trans lactone acid (X) melted at 171-172°.

Found %: C 65.45; 65.55; H 7.63; 7.72

$C_{13}H_{18}O_4$. Calculated %: C 65.52; H 7.53

Found M: 237.1 (titration with NaOH)

$C_{13}H_{18}O_4$. Calculated M: 238.3

The trans Lactone Ester (XI)

The trans lactone acid (X) (0.4 g) was treated with ethereal diazomethane. The liquid reaction product obtained after removal of ether crystallized when treated with petroleum ether. The yield of the trans lactone ester (XI) was 0.4 g. It melted at 64-65.5° (64.5-65.5° after recrystallization from petroleum ether).

Found %: C 66.91; 66.87; H 8.06; 8.14

$C_{14}H_{20}O_4$. Calculated %: C 66.65; H 7.99

Hydrolysis of the trans lactone ester (XI) with 40% caustic potash gave the original trans lactone acid (X), m.p. 170-172°, in low yield.

Attempts to Lactonize the trans Acids (IX) and (XIX)

a) A mixture of 0.25 g of trans-1,2,3,4,5,6,7,8-octahydro-1-methyl-1,2-naphthalenedicarboxylic acid (IX), m.p. 170-171°, and 2.5 ml of glacial acetic acid saturated with dry hydrogen chloride was heated at 60° for one hour. The crystalline residue remaining after removal of acetic acid was crystallized from aqueous acetone and yielded 0.19 g of the original trans acid (IX), m.p. 169-170°.

b) A mixture of 0.15 g of trans-1,2,3,4,5,6,7,8-octahydro-2-methyl-1,2-naphthalenedicarboxylic acid (XIX), m.p. 173-174°, and 2 ml of glacial acetic acid saturated with dry hydrogen chloride was heated at 60° for 90 minutes. Acetic acid was removed under reduced pressure. Two crystallizations of the residue from a mixture of benzene and petroleum ether yielded 0.1 g of an acid of m.p. 171-173°, undepressed by admixture of some of the original trans acid (XIX).

Attempts to Lactonize the trans Acids (XX) and (XXI)

a) A mixture of 0.8 g of trans-1,2,3,5,6,7,8,8a-octahydro-1-methyl-1,2-naphthalenedicarboxylic acid (XX), m.p. 185-186°, and 8 ml of glacial acetic acid saturated with dry hydrogen chloride was heated at 60° for one hour. A thick oil remained after removal of acetic acid by distillation, and this partially crystallized when rubbed in presence of petroleum ether. The crystals were filtered off and washed with petroleum ether. Crystallization from water yielded 0.1 g of a crystalline substance, m.p. 169-171°, undepressed by admixture of the previously prepared trans lactone acid (X). The mother liquor, after treatment with a mixture of diethyl ether and petroleum ether, yielded 0.55 g of a substance that melted at 184-186° after crystallization from 30% aqueous methanol; it was found to be the original trans acid (XX).

b) A mixture of 0.17 g of trans-1,2,3,5,6,7,8,8a-octahydro-2-methyl-1,2-naphthalenedicarboxylic acid (XXI), m.p. 212-213°, and 2 ml of glacial acetic acid saturated with hydrogen chloride was heated at 60° for one hour. The residue remaining after removal of acetic acid under reduced pressure was crystallized twice from 40% aqueous acetone, and yielded 0.13 g of the original trans acid (XXI), m.p. 211-212°.

SUMMARY

1. A study has been made of the lactonization of the cis-1,2,3,5,6,7,8,8a-octahydromethyl-1,2-naphthalenedicarboxylic acids (I) and (II), and also of the cis diesters (VI) and (VII), and evidence relating to the structures of

the resulting cis lactone acids (III) and (XV) has been presented.

2. It has been shown that, of the epimeric trans acids (VIII) and (XX), only the trans acid (VIII) is capable of undergoing lactonization – a result in accord with the spatial configuration of (VIII). The trans acid (XX) and the trans acids (IX) and (XIX), which have inter-ring double bonds, are incapable of lactonization.

3. An examination of molecular models has provided an explanation of the experimentally observed steric hindrance to the lactonization of the trans-octahydromethyl-1,2-naphthalenedicarboxylic acids (IX), (XIX), and (XX).

LITERATURE CITED

[1] I. N. Nazarov, V. F. Kucherov, and V. M. Andreev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, No. 1, 78. *

[2] F. Vocke, Ann. 497, 253 (1932); J. Cook, C. Lawrence, J. Chem. Soc. 1938, 58; I. N. Nazarov and T. D. Nagibina, J. Gen. Chem., 23, 577 (1953). **

[3] R. Adams, E. Gruber, J. Am. Chem. Soc. 60, 2792 (1938).

[4] R. Linstead, H. Rydon, J. Chem. Soc. 1933, 580.

[5] H. Backer, J. Strating, Rec. trav. chim. 60, 391 (1941).

[6] H. Schenk, H. Dutmann, O. Jeger, L. Ružička, Helv. 35, 817 (1952); P. Dietrich, E. Lederer, Helv. 36, 1148 (1953).

[7] I. N. Nazarov, V. F. Kucherov, and V. M. Andreev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, No. 1, 89. ***

Received April 6, 1954

N. D. Zelinsky Institute of Organic Chemistry of the
USSR Academy of Sciences

---

* See Consultants Bureau Translation, p. 67.

** See Consultants Bureau Translation, p. 599.

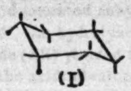
*** See Consultants Bureau Translation, p. 77.

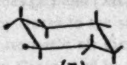
STEREOCHEMISTRY OF CYCLIC COMPOUNDS

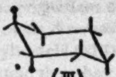
COMMUNICATION 7. GEOMETRIC ISOMERISM OF 4-METHYL-1,2-CYCLOHEXANEDICARBOXYLIC ACIDS

I. N. Nazarov and V. F. Kucherov

The establishment of the fact that, under normal conditions, the cyclohexane molecule exists in the "chair" form [1] makes it possible to obtain a more definite picture of the actual geometric configurations of cyclic compounds. The existence of the cyclohexane molecule in the chair form implies the presence in the molecule of six "equatorial" and six "polar" carbon-hydrogen bonds alternating among themselves. Correspondingly, in the molecule of a disubstituted cyclohexane, the substituents, irrespective of their structural arrangement, may be mutually disposed in three different ways, which may be described as equatorial-polar (e-p) (I), diequatorial (e-e) (II), and dipolar (p-p) (III).


(I)


(II)


(III)

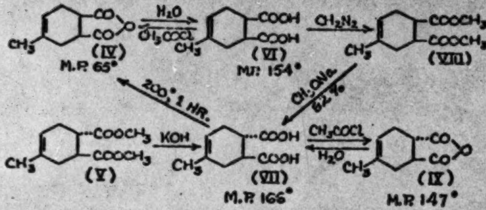
It is not difficult to see that the equatorial-polar arrangement of substituents will correspond to the cis-1,2- trans-1,3-, and cis-1,4-isomers, whereas the other three isomers (trans-1,2-, cis-1,3-, and trans-1,4-isomers) can have either diequatorial or dipolar arrangements of substituents. Thermodynamic calculations for the isomeric dimethylcyclohexanes [2] have shown that the diequatorial arrangement of substituents is considerably more advantageous energetically than the dipolar arrangement. Correspondingly, under normal conditions the trans-1,2-, cis-1,3-, and trans-1,4-dimethylcyclohexanes exist only in the diequatorial forms. These conclusions were later confirmed in a study of the kinetics of the esterification of the isomeric cyclohexanedicarboxylic acids [3], and also in a study of the dissociation constants of various hydroxycyclohexanecarboxylic acids [4]. From dipole-moment measurements it has been proved quite rigorously that the trans-1,4-dichloro (and dibromo) cyclohexanes have the (e-e) disposition of substituents in the solid state [5]. Chemical confirmation of the diequatorial disposition of the carboxyl groups in trans-1,2-cyclohexanedicarboxylic acids is provided by the readiness with which they are dehydrated with formation of meso-trans anhydrides.

These conclusions concerning the higher stability of the equatorial disposition of substituents in disubstituted cyclohexanes have recently been extended with success to the elucidation of the stereochemistry of the complex polycyclic systems of steroids and polyterpenes [6].

The establishment of the absolute geometric configurations of cyclic compounds is one of the main problems of stereochemistry, and we therefore considered that it would be of interest to make a more detailed study of the stereochemistry of trisubstituted cyclohexanes. As a suitable subject for investigation we selected 4-methyl-1,2-cyclohexanedicarboxylic acid.

For the preparation of all of the four stereoisomers of this acid that are predicted by theory, the most convenient method was that based on the diene condensation of isoprene with maleic anhydride [7,8] and with fumaric ester [10], followed by hydrogenation of the resulting adducts. The chemical transformations of our starting materials may be presented as follows: (See top of following page).

When studying the hydrogenation of the anhydride of cis-4-methyl-4-cyclohexane-1,2-dicarboxylic acid (IV), Craig [8] found that a mixture of two isomers was formed (separated by crystallization in the form of the corresponding acids), and that one of these readily isomerized to the other when heated with dibutylaniline. Comparing these results with the stereochemical transformations of adducts obtained by the condensation of cis- and trans-piperylenes with maleic anhydride, Craig concluded that the isomer was trans-4-methyl-cis,cis-1,2-cyclohexanedicarboxylic acid.

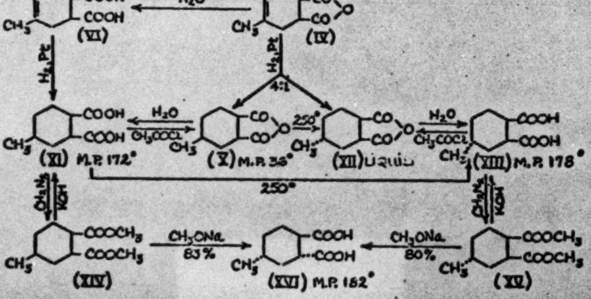


We have made a detailed study of the hydrogenation of the cis and trans anhydrides (IV) and (IX), and also of the corresponding acids (VI) and (VII).

It was found that hydrogenation of the cis anhydride (IV) in benzene solution over platinum oxide yielded a mixture of crystalline and liquid saturated anhydrides (X) and (XII) in the proportions of 4 : 1 approximately. The crystalline anhydride (X), m.p. 36°, was hydrolyzed by water to the saturated cis dicarboxylic acid (XI), m.p. 172-172.5°, whereas the liquid anhydride (XII) yielded the isomeric cis dicarboxylic acid (XIII), m.p. 178-179°. Both of these isomeric acids correspond to the acids obtained by Craig, and in admixture they show a great depression in melting point. Hydrogenation of the cis acid (VI) over platinum oxide in methanol was found to proceed much more selectively, and the main product was the acid (XI) with only a slight amount of the isomeric acid (XIII) as impurity.

This interesting fact is an indication that the screening of the double bond in the cis acid (VI), which is effected by the two cis-ortho carboxyl groups, is more effective than that of the double bond in the anhydride (IV), in which it is effected by the cis anhydride grouping. For this reason the addition of hydrogen to the cis acid (VI) occurs almost exclusively from the side opposite to the carboxyl groups with formation of the saturated acid (XI), in which the methyl group is on the same side as the carboxyl groups. This result is in full accord with data that indicate that catalytic hydrogenation is a reaction of cis addition of hydrogen.

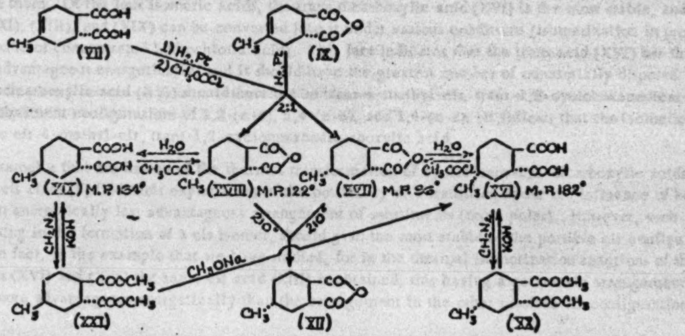
A study of the thermal stabilities of the isomeric cis dicarboxylic acids (XI) and (XIII) and of their anhydrides (X) and (XII) has shown that, when the acid (XI), or the corresponding anhydride (X), is heated for a short time at 240-250°, a mixture of isomeric anhydrides (X) and (XII) is formed, with a great predominance of the latter. When this mixture is hydrolyzed, the pure cis dicarboxylic acid (XIII) can be isolated in good yield by crystallization from aqueous methanol. These results indicate the high stability of the cis acid (XIII), as compared with the isomeric cis acid (XI), and are in accord with the results obtained for the adducts formed by cis- and trans-piperylenes with maleic anhydride [8].



When treated with ethereal diazomethane, the isomeric cis dicarboxylic acids (XI) and (XIII) yielded the corresponding cis diesters (XIV) and (XV). Isomerization of these cis diesters in presence of sodium methoxide yielded, in each case, the trans acid (XVI), m.p. 181-182°, which was converted by acetyl chloride into the trans anhydride (XVII), m.p. 96-97°. This fact indicates that in the isomerization of the diesters (XIV) and (XV) in presence of sodium methoxide, different carbon atoms are affected. Isomerization of the diester (XIV) is accompanied by rearrangement of the bonds at C-1, whereas the diester (XV) undergoes a like change at C-2, the result being that the same trans acid (XVI) is formed.

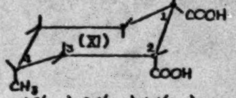
The formation of a single trans isomer, probably corresponding to the more stable configuration, prompted us to make a detailed study of the hydrogenation of the unsaturated trans acid (VII) and its anhydride (IX). As was to be expected, in neither of these cases was the hydrogenation selective.

It was found that in the hydrogenation of the trans anhydride (IX) in benzene solution over platinum oxide, a crystalline mixture of unsaturated trans anhydrides was formed. By treatment of this mixture with ether we succeeded in isolating a pure trans anhydride (XVIII), m.p. 121-122° in an amount equal to about one-third of the mixture taken. This trans anhydride differed from the trans anhydride (XVII) obtained from the trans acid (XVI), and it gave by hydrolysis the new trans acid (XIX), m.p. 164-165°. The crystalline mixture remaining after separation of the trans anhydride (XVIII) was crystallized from petroleum ether, and an apparently homogeneous crystalline product was obtained which melted over a range, 74-77°. Hydrolysis of this product with water yielded a mixture of acids, from which the trans acid (XVI) was isolated after three crystallizations from aqueous methanol. By crystallization from petroleum ether of a known mixture of the isomeric trans anhydrides (XVII) and (XVIII) it was shown that the crystalline product of m.p. 74-77° corresponded to a mixture of equal amounts of these trans anhydrides. Hence, in the hydrogenation of the trans anhydride (IX) a mixture of the isomeric saturated trans anhydrides (XVII) and (XVIII) is formed in the proportions of 1 : 2 approximately. The same ratio of isomers is obtained also in the hydrogenation of the trans acid (VII).

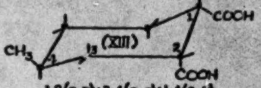


The isomeric trans dicarboxylic acids (XVI) and (XIX) were converted by reaction with diazomethane into the corresponding isomeric trans diesters (XX) and (XXI). It was found that, when boiled with sodium methoxide, the trans diester (XXI) was converted in good yield into the trans acid (XVI). The same transformation was readily effected also by heating the trans dicarboxylic acid (XIX) with concentrated hydrochloric acid. On the other hand, the isomeric trans anhydrides (XVII) and (XVIII), by simple heating at 210° for 30 minutes, were almost quantitatively isomerized into the same cis anhydride (XII), corresponding to trans-4-methyl-cis,cis-1,2-cyclohexanedicarboxylic acid (XIII).

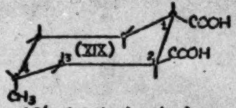
When all of our results on the mutual transformations of the four isomeric 4-methyl-1,2-cyclohexane dicarboxylic acids are examined in the light of the theory of the "equatorial-polar" disposition of substituents, it is found that the geometric configurations of these acids can be established with exactness. The four isomeric 4-methyl-1,2-cyclohexanedicarboxylic acids can be represented by the following models:



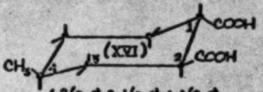
1,2(e-p); 2,4(p-p); 1,4(e-p)



1,2(e-p); 2,4(p-e); 1,4(e-e)



1,2(e-e); 2,4(e-p); 1,4(e-p)



1,2(e-e); 2,4(e-e); 1,4(e-e)

For the two isomeric cis dicarboxylic acids (XI) and (XIII), the cis configuration of the 1- and 2-carboxyl groups (e-p) follows from the method of preparation (diene synthesis). On the assumption that the more equatorial arrangement of substituents will correspond to the more stable form, it follows that the more stable cis dicarboxylic acid (XIII) of m.p. 178° will have substituent configurations of 1,2-(e-p), 2,4-(p-e), and 1,4-(e-e) and will be trans-4-methyl-cis, cis-1,2-cyclohexanedicarboxylic acid. The isomeric cis acid (XI) will have the thermodynamically less advantageous substituent configurations of 1,2-(e-p), 2,4-(p-p), and 1,4-(e-p), amd will be cis-4-methyl-cis, cis-1,2-cyclohexanedicarboxylic acid.

The diequatorial configuration of the trans-1,2 carboxyl groups in the trans acids (XVI) and (XIX) follows from the method of preparation (diene synthesis with fumaric ester) and from the readiness with which trans anhydrides are formed from them. Of the four isomeric acids, the trans dicarboxylic acid (XVI) is the most stable, and the other three acids (XI), (XIII), and (XIX) can be converted into it under various conditions (isomerization in presence of sodium methoxide or concentrated hydrochloric acid). This fact indicates that the trans acid (XVI) has the structure that is most advantageous energetically, and it should have the greatest number of equatorially disposed substituents. The transdicarboxylic acid (XVI) should therefore be trans-4-methyl-cis, trans-1,2-cyclohexanedicarboxylic acid, having substituent configurations of 1,2-(e-e), 2,4-(e-e), and 1,4-(e-e). It follows that the isomeric trans acid (XIX) will be cis-4-methyl-cis, trans-1,2-cyclohexanedicarboxylic acid.

The numerous examples that are known of the thermal transformation of cyclic trans-1,2-dicarboxylic acids into the corresponding cis acids [9] find their explanation in the possibility of a transition under the influence of heat into a system having an energetically less advantageous arrangement of substituents (more polar). However, such a transformation, resulting in the formation of a cis isomer, should give the most stable of the possible cis configurations. This occurs, in fact, in the example that we have studied, for in the thermal isomerization reactions of the trans dicarboxylic acids (XVI) and (XIX) the same cis acid (XIII) is obtained, this having a geometric arrangement of substituents that is more advantageous energetically than the arrangement in the other possible cis configuration.

EXPERIMENTAL

Anhydride of trans-4-Methyl-cyclohexene-1,2-dicarboxylic Acid

A mixture of 2 g of the trans acid (VII) [10], m.p. 165-166°, and 20 ml of acetyl chloride was boiled until solution was complete (1.5-2 hours). The crystals remaining after removal of acetyl chloride by distillation were washed on the filter with a mixture of diethyl ether and petroleum ether (1 : 2). The product was 1.75 g of a substance of m.p. 141-143°. Two crystallizations from a mixture of benzene and petroleum ether (1 : 3) yielded the pure trans anhydride (IX), m.p. 146-147°.

Found %: C 65,11; 65,24; H 6,14; 6,15
$C_9H_{10}O_3$. Calculated %: C 65,04; H 6,06

When boiled with water, the trans anhydride (IX) gave a quantitative yield of the original trans acid (VII), m.p. 165-166°.

Thermal Isomerization of the trans Anhydride (IX)

The trans anhydride (IX) (1.2 g) was heated in an atmosphere of nitrogen at 200-210° for one hour. The light-brown melt solidified completely when cooled, and it had a melting point of 60-64°. Crystallization from a mixture of diethyl ether and petroleum ether yielded 0.8 g of a crystalline substance, m.p. 64-65°, undepressed by admixture of pure cis anhydride (IV) [7].

Hydrogenation of the cis-Anhydride (IV)

The cis anhydride (IV) [7] of m.p. 64-65° (7.0 g) was dissolved in 50 ml of absolute benzene and hydrogenated over platinum oxide. One molecular proportion of hydrogen (950 ml at 0° and 760 mm) was absorbed. The benzene was distilled off under reduced pressure, and the residue was dissolved in 20 ml of petroleum ether. The solution was left overnight under ice cooling. The crystals that separated were washed on the filter with a cold mixture of diethyl ether and petroleum ether (1 : 5), and 3.8 g of crystals melting at 33.5-35° was obtained. The solvents were distilled from the mother liquor, and the residue was dissolved in petroleum ether containing a little diethyl ether. The solution was cooled with solid carbon dioxide, and a further 0.7 g of crystals melting at 33-34.5° separated. The total yield of the saturated crystalline cis anhydride (X) was 4.5 g. After being crystallized from a mixture of diethyl ether and petroleum ether (1 : 2), the substance had a constant melting point of 35-36.5°.

Found %: C 64.19; 64.00; H 7.32; 7.10

$C_9H_{12}O_3$. Calculated %: C 64.26; H 7.20

The liquid residue remaining after separation of the cis anhydride (X) was hydrolyzed at the boil with 7 ml of water. The crystals obtained when the mixture cooled were washed on the filter with 10% aqueous methanol (1.9 g, m.p. 140-160°). Fractional crystallization from 50% methanol yielded 1.0 g of crystals melting at 174-177°. Recrystallization from 50% methanol yielded 0.85 g of the pure dicarboxylic acid (XIII), melting with decomposition at 177-178°. The trans-4-methyl-cis,cis-1,2-cyclohexanedicarboxylic acid described by Craig [8] melted at 177-178°.

cis-4-Methyl-cis,cis-1,2-cyclohexanedicarboxylic Acid (XI)

A mixture of 0.5 g of the cis anhydride (X), m.p. 35-36°, and 2 ml of water was boiled until solution was complete. When the solution was cool, 0.52 g of an acid, m.p. 171-173°, separated. Crystallization from water yielded the pure cis dicarboxylic acid (XI), m.p. 172-173°, identical with the acid described previously [8] and giving a depression of melting point in admixture with the cis dicarboxylic acid (XIII).

Found %: C 58.24; 58.15; H 7.61; 7.63

$C_9H_{14}O_4$ Calculated %: C 58.05; H 7.59

When the cis dicarboxylic acid (XI) was boiled with acetyl chloride, a quantitative yield was obtained of the pure original anhydride (X), m.p. 34-36°.

Thermal Isomerization of the Anhydride of cis-4-Methyl-cis,cis-1,2-cyclohexanedicarboxylic Acid (X)

The cis anhydride (X) of m.p. 35-36° (3.8 g) was heated at 200-210° for 90 minutes in an atmosphere of nitrogen. Heating was continued for a further thirty minutes under reduced pressure at 240-250°, and the substance was then slowly distilled under reduced pressure at a bath temperature of 230-235°. The product was 2.4 g of a colorless viscous liquid (n_D^{20} 1.4795), and when this was boiled with water it yielded 2.2 g of a crystalline acid melting at 173-175°. Crystallization from 50% methanol yielded 1.8 g of pure trans-4-methyl-cis,cis-1,2-cyclohexanedicarboxylic acid (XIII), melting with decomposition at 177-178° and identical with the acid prepared previously.

Anhydride of trans-4-Methyl-cis,cis-1,2-cyclohexanedicarboxylic Acid (XII)

A mixture of 2.6 g of the dicarboxylic acid (XIII), m.p. 177-178°, and 25 ml of acetyl chloride was boiled until solution was complete (one hour). After removal of acetyl chloride under reduced pressure, the liquid reaction product, which did not crystallize when cooled and when treated with solvents, was vacuum-distilled. The product was 2.1 g of the cis anhydride (XII) in the form of a colorless viscous liquid, b.p. 127-128° (4 mm) and n_D^{20} 1.4790.

Found %: C 64.55; 64.39; H 7.33; 7.33

$C_9H_{12}O_3$ Calculated %: C 64.26; H 7.20

When boiled with water, the cis anhydride (XII) gave a quantitative yield of the original cis dicarboxylic aicd(XIII), which melted with decomposition at 176-178°.

Hydrogenation of cis-4-Methyl-4-cyclohexene-1,2-dicarboxylic Acid (VI)

The cis acid (VI) [7] of m.p. 154-155° (5.4 g) was dissolved in 50 ml of absolute methanol and hydrogenated over platinum oxide. When one molecular proportion of hydrogen (640 ml) had been absorbed the methanol was distilled off and 5.3 g of crystals melting at 160-166° was obtained. Recrystallization from 12 ml of 50% aqueous methanol yielded 3.8 g of the pure dicarboxylic acid (XI), melting at 172-173° and identical with the acid obtained previously. Evaporation of the mother liquor to dryness and two recrystallizations of the residue from 50% aqueous methanol yielded a further 0.8 g of the pure dicarboxylic acid (XI), m p. 172-173°. By fractional crystallization of the residues from aqueous methanol it was found possible to isolate about 50 mg of an acid melting at 176-177° and identical with the isomeric dicarboxylic acid (XIII) obtained previously.

Dimethyl Ester of cis-4-Methyl-cis,cis-1,2-cyclohexanedicarboxylic Acid (XIV)

A small excess of ethereal diazomethane was added to a suspension of 5 g of the dicarboxylic acid (XI), m.p. 171-173°, in 50 ml of ether. After removal of ether, the liquid reaction product was vacuum-distilled, and yielded 5.1 g of the cis diester (XIV), b.p. 110-110.5° (4 mm); n_D^{20} 1,4575; d_4^{20} 1,0782; found MR 54,11; calculated MR 54,17:

Found %: C 61,46; 61,51; H 8.31; 8,33
$C_{11}H_{18}O_4$. Calculated %: C 61,66; H 8,47

Hydrolysis of the cis diester (XIV) with 20% aqueous caustic potash yielded the original cis dicarboxylic acid (XI), m.p. 171-173°.

Dimethyl Ester of trans-4-Methyl-cis,cis-1,2-cyclohexanedicarboxylic Acid (XV)

This was prepared by the procedure of the previous experiment from 3.6 g of the isomeric dicarboxylic acid (XIII), m.p. 176-178°. The distillation yielded 3.6 g of the cis diester (XV), b.p. 105-105.5° (3 mm); n_D^{20} 1,4572; d_4^{20} 1,0796; found M R 54,12; calculated MR 54,17;

Found %: C 61.62; 61.71; H 8.55, 8.55
$C_{11}H_{18}O_4$ Calculated %: C 61.66; H 8.47

Hydrolysis of the cis diester (XV) with 20% caustic potash gave a good yield of the original cis dicarboxylic acid (XIII), m.p. 177-178°.

trans-4-Methyl-cis,trans-1,2-cyclohexanedicarboxylic Acid (XVI)

a) The cis diester (XIV) (2.1 g) was added to a solution of 4.7 g of sodium in 120 ml of absolute methanol, and the solution was boiled for 15 hours. The methanol was distilled off under reduced pressure, and the residue was dissolved in 40 ml of water. The solution was treated with charcoal and filtered, and was then evaporated in a porcelain dish on a water bath until a thick slurry was obtained. The precipitated salts were filtered off, washed on the filter with a little methanol, and dissolved in 10 ml of water. The solution was acidified with concentrated hydrochloric acid, and 1.5 g (83%) of a crystalline acid melting at 179-180° was obtained. Crystallization from 30% aqueous methanol yielded the pure trans dicarboxylic acid (XVI), which had a constant melting point of 181-182°.

Found %: C 58,05; 58,09; H 7.83, 7.66
$C_9H_{14}O_4$. Calculated %: C 58,05; H 7.58

b) In a similar way, 2.8 g of the cis diester (XV) was boiled for 15 hours with a solution of 6.2 g of sodium in 160 ml of absolute methanol, and 1.8 g of a crystalline acid melting at 178-180° was isolated. After crystallization from 40% methanol it melted at 180-181°, and there was no depression in a mixture test with the trans dicarboxylic acid (XVI) obtained in the previous experiment. It gave a depression with the cis acid (XIII) (160-164°).

Anhydride of trans-4-Methyl-cis,trans-1,2-cyclohexanedicarboxylic Acid (XVII)

A mixture of 1.0 g of the trans dicarboxylic acid (XVI), m.p. 180-182°, and 20 ml of acetyl chloride was boiled until solution was complete (one hour). The excess of acetyl chloride was distilled off, and the liquid residue was heated in a vacuum at 80-85° for 20 minutes. Treatment with petroleum ether yielded a crystalline substance, which was washed on the filter with a cold mixture of diethyl ether and petroleum ether (1 : 5). The product was 0.65 g of a crystalline substance melting at 88-90°. After crystallization from a little ether, the trans anhydride (XVII) had a constant melting point of 96-97°.

Found %: C 64.29, 64.18; H 7.22, 7.25
$C_9H_{12}O_3$ Calculated %: C 64.26; H 7.20

When the trans anhydride (XVII) was boiled with water, a quantitative yield of the original trans dicarboxylic acid (XVI), m.p. 180-181°, was obtained.

Hydrogenation of the Anhydride of trans-4-Methyl-4-cyclohexene-1,2-dicarboxylic Acid (IX)

The trans anhydride (IX) (5.5 g) was dissolved in 80 ml of cryoscopic benzene and hydrogenated over platinum oxide. The amount of hydrogen absorbed was 800 ml at 20° and 745 mm. The benzene was distilled off, and the liquid hydrogenation product that then remained gradually crystallized on standing. The crystalline substance was treated with a little warm benzene, and the undissolved part (0.3 g melting at 158-164°) was filtered off. The benzene was removed under reduced pressure, and the crystalline residue was washed on the filter with 50 ml of absolute ether. The product was 1.45 g of an ether-insoluble substance, m.p. 110-115°. Two recrystallizations of this from a small amount of a mixture of benzene and ether yielded the pure trans anhydride (XVIII) (1.2 g), which had a constant melting point of 121.5-122.5°.

Found %: C 64.49, 64.28; H 7.41, 7.24
$C_9H_{12}O_3$ Calculated %: C 64.26; H 7.20

The ether solution remaining after separation of the trans anhydride (XVIII) was evaporated to dryness, and 3.55 g of a crystalline substance melting at 65-75° was obtained. This substance was heated with 200 ml of petroleum ether, and the undissolved residue was filtered off. A substance of m.p. 90-140° (0.4 g) was obtained, and from this, after washing on the filter with a little ether and crystallization from 40% aqueous methanol, 0.15 g of the trans dicarboxylic acid (XVI), m.p. 180-181°, was isolated.

The petroleum ether solution was evaporated to small bulk, and 2.15 g of a crystalline substance, m.p. 72-75°, was obtained. The product was readily soluble in ether, and it crystallized from petroleum ether in the form of apparently homogeneous needles having a melting range of 73-77°. Attempts to isolate individual substances by crystallization were unsuccessful, and 1.2 g of this crystalline mixture was hydrolyzed at the boil with 5 ml of water. The resulting crystalline mixture of acids (m.p. 168-175°) was crystallized three times from 40% methanol, and 0.5 g of the trans dicarboxylic acid (XVI) was obtained. It melted at 179-181°, and gave no depression in admixture with an authentic sample.

A mixture of equal amounts of the pure trans anhydrides (XVII) and (XVIII) was crystallized from petroleum ether and then melted at 74-77°; there was no depression in a mixture test with the mixture of anhydrides obtained in the experiment described above.

Hydrogenation of trans-4-Methyl-4-cyclohexene-1,2-dicarboxylic Acid (VII)

The trans acid (VII) (4.2 g) was dissolved in 40 ml of methanol and hydrogenated over platinum oxide. One molecular proportion of hydrogen (515 ml) was absorbed. The thick liquid remaining after removal of methanol rapidly solidified when a little water was added. The product was 4.1 g of a mixture of acids melting at 160-165°, and it was not found possible to separate the acids by crystallization. The acids were converted into their anhydrides by boiling the mixture with 40 ml of acetyl chloride for two hours. The residue remaining after removal of acetyl chloride was treated with petroleum ether, and 2.85 g of a crystalline mixture of anhydrides melting at 73-90° was obtained. Treatment of the mixture with ether yielded 0.8 g of the pure trans anhydride (XVIII), m.p. 121-122°, and 1.6 g of an unresolvable mixture of the trans anhydrides (XVII) and (XVIII), m.p. 74-76°, which was hydrolyzed to a mixture of acids. Three crystallizations of the mixture of acids from 40% methanol yielded 0.6 g of the pure trans dicarboxylic acid (XVI), m.p. 180-181°.

cis-4-Methyl-cis,trans-1,2-cyclohexanedicarboxylic Acid (XIX)

A mixture of 0.6 g of the trans anhydride (XVIII), m.p. 121-122°, and 2.5 ml of water was boiled until solution was complete (five minutes). On cooling, the solution yielded 0.65 g of crystals of the trans dicarboxylic acid (XIX), m.p. 161-162°. After being crystallized from 20% aqueous methanol they had a constant melting point of 162-164°.

Found %: C 57.82; 57.83; H 7.45; 7.59
$C_9H_{14}O_4$ Calculated %: C 58.05; H 7.58

When treated with excess of acetyl chloride, the dicarboxylic acid (XIX) was converted in good yield into the original trans anhydride (XVIII), m.p. 120-121°.

Dimethyl Ester of trans-4-Methyl-cis,trans-1,2-cyclohexanedicarboxylic Acid (XX)

Treatment of 3 g of the trans dicarboxylic acid (XVI), m.p. 181-182°, with excess of ethereal diazomethane, followed by vacuum distillation, gave 3.1 g of the trans diester (XX), b.p. 110-110.5° (4 mm); n_D^{20} 1.4535; d_4^{20} 1.0660; found MR 54.38; calculated MR 54.11.

	Found %:	C 61.59, 61.55;	H 8.65, 8.55
$C_{11}H_{18}O_4$.	Calculated %:	C 61.66;	H 8.47

Hydrolysis of the trans diester (XX) with 20% caustic potash gave a good yield of the original trans dicarboxylic acid (XVI), m.p. 180-181°.

Dimethyl Ester of cis-4-Methyl-cis,trans-1,2-cyclohexanedicarboxylic Acid (XXI)

By the procedure of the previous experiment 1.0 g of the trans dicarboxylic acid (XIX), m.p. 163-164°, yielded 1.05 g of the trans diester (XXI), b.p. 111° (5 mm); n_D^{20} 1.4570; d_4^{20} 1.0800; found MR 54.03; calculated MR 54.11.

	Found %:	C 61.38, 61.45;	H 8.52, 8.64
$C_{11}H_{18}O_4$.	Calculated %:	C 61.66;	H 8.47

Hydrolysis of the trans diester (XXI) with 20% caustic potash gave the original trans acid (XIX), m.p. 162--164°.

Isomerization of the trans Dicarboxylic Acid (XIX) and its Diester (XXI)

a) A mixture of 0.5 g of the trans dicarboxylic acid (XIX), m.p. 163-164°, and 5 ml of concentrated hydrochloric acid was heated in a sealed glass tube at 170-175° for seven hours. Hydrochloric acid was distilled off, and crystallization of the residue from 40% aqueous methanol yielded 0.3 g of acid melting at 181-182°, identical with the trans acid (XVI).

b) The trans diester (XXI) (0.4 g) was added to a solution of 1 g of sodium in 30 ml of absolute methanol, and the mixture was boiled for 15 hours. The methanol was distilled off, and the residue was dissolved in 10 ml of water. The solution was evaporated down to a thick slurry in a porcelain dish. The precipitate of salts was filtered off, washed with methanol, and dissolved in 2 ml of water. Acidification of the solution with concentrated hydrochloric acid yielded 0.3 g of the trans acid (XVI), m.p. 180-181°, undepressed by admixture of a known sample.

Thermal Isomerization of the trans Anhydrides (XVII) and (XVIII)

a) The trans anhydride (XVII) of m.p. 96-97° (0.5 g) was heated in nitrogen at low pressure for one hour at 210-215°. The reaction product was vacuum-distilled at a bath temperature of 200-205° (n_D^{20} 1.4795) and then hydrolyzed at the boil with 2 ml of water. The product was 0.4 g of a crystalline acid melting at 173-175°. After being crystallized from 50% aqueous methanol, it melted at 177-178°, and there was no depression in a mixture test with a pure sample of the cis dicarboxylic acid (XIII).

b) Similarly, 0.5 g of the trans anhydride (XVIII), m.p. 121-122°, after being heated and vacuum-distilled, yielded a liquid having n_D^{20} 1.4790. Hydrolysis gave 0.4 g of an acid melting at 175-176°. Crystallization from 50% methanol gave the pure cis dicarboxylic acid (XIII), m.p. 177-178°, undepressed by an authentic sample.

SUMMARY

1. All four theoretically possible isomers of 4-methyl-1,2-cyclohexanedicarboxylic acid have been prepared by the hydrogenation of cis- and trans-4-methyl-4-cyclohexene-1,2-dicarboxylic acids (VI) and (VII) and of their anhydrides (IV) and (IX).

2. A study has been made of the mutual stereochemical conversions of these four isomers under the influence of heat and of isomerization agents, and this has enabled us to determine the relative stabilities of the individual forms of the cis and trans series.

3. The geometric configurations of all four isomeric 4-methyl-1,2-cyclohexanedicarboxylic acids have been examined on the basis of the theory of the "equatorial-polar" arrangement of substituents.

Received April 6, 1954 N. D. Zelinsky Institute of Organic Chemistry of the USSR Academy of Sciences

LITERATURE CITED

[1]. O. Hassel, Acta chim. Scand. 1, 149, 929, (1947); R. Rasmussen, J. Chem. Phys. 11, 249 (1943).

[2]. C. Beckett, K. Pitzer, R. Spitzer, J. Am. Chem. Soc. 69, 2488 (1947).

6

[3] H. Smith, F. Byrne, J. Am. Chem. Soc. 72, 4406 (1950).

[4] M. Kilpatrick, J. Morse, J. Am. Chem Soc. 75, 1846 (1953).

[5] K. Kozima, T. Yoshino, J. Am. Chem. Soc. 75, 166 (1953).

[6] D. Barton, G. Schmeidler, J. Chem. Soc., 1948, 1197; D. Barton, Experientia 6, 316 (1950).

[7] O. Diels, K. Alder, Ann. 470, 62 (1929).

[8] D. Craig, J. Am. Chem. Soc. 72, 1678 (1950).

[9] I. N. Nazarov and V. F. Kucherov, Bull. Acad. Sci. USSR, Div. Chem. Sci., (1952) No. 2, 289 *; I. N. Nazarov and V. F. Kucherov, Bull. Acad. Sci. USSR, Div. Chem. Sci. (1954), No. 2, 329. **

[10] A. Petrov and N. Sopov, Collected Papers on General Chemistry, Vol. 2, (1953), p. 853

* Consultant's Bureau Translation, p. 301

** Consultant's Bureau Translation, p. 269

BLANK
PAGE

CATALYTIC AMINATION OF ALCOHOLS

M.A. Popov and N.I. Shuikin

The catalytic amination of alcohols has been the subject of numerous investigations. The investigators have usually confined themselves to a search for efficient catalysts and the determination of optimum conditions for preparing amines. Only occasionally have they attempted to determine what intermediate compounds are formed in the conversion of the alcohol into an amine. The solution of this problem, however, would be valuable, not only for the theory of catalysis, but also as an aid to the selection of the catalyst and reaction conditions in the synthesis of amines.

Sabatier and Maihle [1], on the basis of experiments on the amination of alcohols in presence of thorium oxide, considered that unstable alkyl thorates were first formed, and these then reacted with ammonia, giving primary amines. The latter, in their turn, also reacted with alkyl thorates giving secondary amines, and in a similar way the secondary amines were converted into tertiary amines. According to Sabatier, therefore, amination proceeds in two stages: first the alcohol reacts with the metal oxide, and then the esterlike compound formed reacts with ammonia with elimination of water and formation of an amine. For this reason these authors used various metal oxides as catalysts for the amination of alcohols.

Similar ideas have been expressed by other investigators, who have used metal oxides as catalysts for the amination of alcohols and consider that the formation of an intermediate compound between the alcohol and the catalyst must occur [2]. Shuikin, Balandin, and Plotkin, in a paper on the amination of ethanol [3], have expressed a different view, namely, that the conversion of the alcohol into the amine occurs by the redistribution of bonds on the surface of the active centers of the catalyst, without formation of intermediate compounds.

Schwegler and Adkins [4], who made use of Mignonac's ideas concerning the reactions of aldehydes and ketones with ammonia, considered that aldehydes or ketones are formed intermediately in the amination of alcohols, and these then react with ammonia. The resulting imines are reduced by hydrogen, giving primary amines. Similarly, reaction of the primary amines with carbonyl compounds yields secondary amines, and from the secondary amines tertiary amines are formed. Since the rates of these reactions vary, carbonyl compounds are found in the condensate. According to this scheme, tertiary alcohols, being unable to yield either aldehydes or ketones, cannot give amines. Baum [5] considers that in the amination of alcohols ethers are first formed, and these then react with ammonia with formation of primary and secondary amines. On this scheme the formation of tertiary amines will be improbable, and its author suggests, therefore, that tertiary amines arise " in the usual way" from secondary amines and alcohols.

We set ourselves the task of determining experimentally whether or not these reaction schemes for the conversion of alcohols into amines were in accord with the actual course of the reactions. We have investigated the catalytic amination of alcohols, aldehydes, ketones, and ethers, the substances used being ethanol, 2-propanol, 1- and 2-butanols, cyclohexanol, acetaldehyde, butyraldehyde, acetone, 2-butanone, cyclohexanone, diethyl ether, butyl ethyl ether, and diisopentyl ether. The results for the amination of 1- and 2-butanols and of the ketones are taken from our previous papers [6]. Platinized silica gel and activated wood charcoal were used as catalysts; these have been shown to have high amination activity [7].

EXPERIMENTAL

The properties of the alcohols, aldehydes, and ethers used in the investigation are given in Table 1.

In the experiments, the vapor of the organic compound together with ammonia — and for the amination of aldehydes and ketones, also an excess of hydrogen — was passed into the catalysis tube, which was situated in an electric furnace. In each experiment the amount of catalyst taken was 100 ml; the preparation of the catalysts has been described previously [7]. The duration of each experiment was one hour.

The liquid part of the catalyzate was dried, and the contents of primary, secondary, and tertiary amines were determined by Weber and Wilson's method, ammonia being first removed by Francois' method. However, the use of only the analytical method for the investigation of the complex condensates obtained in the amination of alcohols and carbonyl compounds is inadequate, for at high reaction temperatures other basic substances may be formed. In some experiments, therefore, the isolation and investigation of the amines was carried out. The amines isolated were converted into chloroplatinates, which were analyzed for platinum.

TABLE 1

Properties of Starting Materials

Substance	B.p. (°C)	Pressure (mm Hg)	d_4^{20}	n_D^{20}	Literature references
Ethanol	78	758	0.8792	1.3611	[8, 9, 10]
2-Propanol	82	756	0.7855	1.3772	[8, 11]
Acetaldehyde	21	758	0.7836	1.3320	[12]
Butyraldehyde	74	752	0.8166	1.3842	[13]
Diethyl ether	35	752	0.7134	1.3540	[14]
Butyl ethyl ether	92	752	0.7457	1.3770	[15]
Diisopentyl ether	171	754	0.7724	–	[16, 17]

Information on the experimental conditions and the contents of amines in the condensates is given in Tables 2 and 3.

Elementary-analysis results for amines isolated from the amination condensates of ethanol, the butanols, and the ketones are given in Table 4. The boiling points of the amines obtained and the platinum contents of their chloroplatinates are given in Table 5.

In the reductive amination of acetaldehyde over platinized silica gel and over active charcoal, solid condensates were obtained, and investigation showed them to be aldehyde-ammonia. The amines were extracted with hydrochloric acid from 49 g of the condensate obtained in the reductive amination of butyraldehyde over platinized silica gel. They were then liberated with caustic alkali, dried, and fractionally distilled, when the following fractions were obtained:

Fraction I	B.p. 75-77° (754 mm); 2.7 g
Fraction II	B.p. 157-162° (754 mm); 2.8 g
Fraction III	B.p. 210-220° (754 mm); 0.5 g

TABLE 2

Experimental Conditions for the Catalytic Amination of Alcohols, Carbonyl Compounds, and Ethers

Original substance	Platinum catalyst					Active charcoal catalyst				
	Temperature of experiment (°C)	Amount taken (g)		Amount of condensate (g)	Nitrogen content of amines (%)	Temperature of experiment (°C)	Amount taken (g)		Amount of condensate (g)	Nitrogen content of amines (%)
		Organic substance	Ammonia				Organic substance	Ammonia		
Ethanol	400	10.5	14.5	11.0	2.1	450	12.5	12.3	11.0	5.3
2-Propanol	300	15.7	10.8	17.5	1.4	450	15.7	10.8	13.0	7.7
1-Butanol	450	18.1	20.5	6.6	5.9	350	20.7	11.0	8.0	3.3
2-Butanol	300	16.8	13.4	12.0	1.4	350	16.0	14.8	11.0	3.6
Cyclohexanol	320	9.0	4.9	6.0	3.8	320	9.7	4.9	7.3	3.3
Acetaldehyde	Does not give amines					Does not give amines				
Butyraldehyde	400	8.1	4.0	7.7	2.4	350	8.2	4.1	8.6	8.3
Acetone	300	6.0	2.6	5.2	6.5	450	8.0	4.1	6.5	6.4
2-Butanone	290	6.4	4.5	6.7	2.9	350	8.1	5.0	5.2	2.4
Cyclohexanone	320	9.0	5.1	8.0	2.2	350	9.0	4.5	9.1	3.2
Diethyl ether	400	16.4	12.4	10.0	0.45	450	14.9	10.7	8.0	0.9
Butyl ethyl ether	450	11.9	7.3	9.2	1.03	–	–	–	–	–
Diisopentyl ether	450	16.1	5.9	9.9	1.03	450	19.1	8.3	16.6	1.02

The elementary analyses of these fractions were (%):

Fraction I : C 65.62; H 15.23; N 19.10
Fraction II : C 74.13; H 15.12; N 11.08
Fraction III : C 77.78; H 14.80; N 7.48

The results indicated that Fraction I was mainly butylamine, Fraction II mainly dibutylamine, and Fraction III mainly tributylamine.

TABLE 3

Amine Contents in Condensates from the Amination of Alcohols and the Corresponding Carbonyl Compounds

Original Substance	Platinum catalyst				Active charcoal catalyst			
	Amine content of condensate (%)				Amine content of condensate (%)			
	Primary	Secondary	Tertiary	Total	Primary	Secondary	Tertiary	Total
Ethanol	5.9	1.6	0.9	8.4	10.6	6.5	5.0	22.1
2-Propanol	0.8	3.6	7.2	11.6	7.2	26.4	24.0	57.6
1-Butanol	5.5	4.6	57.7	67.8	3.4	20.1	6.3	29.8
2-Butanol	7.3	–	–	7.3	13.3	–	14.2	27.5
Cyclohexanol	26.4	–	–	26.4	22.4	–	–	22.4
Acetaldehyde	Does not give amines				Does not give amines			
Butyraldehyde	5.4	5.6	1.0	12.0	–	–	6.2	6.2
Acetone	27.5	–	–	27.5	26.9	–	–	26.9
2-Butanone	15.1	–	–	15.1	12.5	–	–	12.5
Cyclohexanone	15.4	–	–	15.4	22.4	–	—	22.4

TABLE 4

Results of the Elementary Analysis of the Amines Isolated

Amine	Found %			Calculated %		
	C	H	N	C	H	N
Ethylamine	53.13	15.64	31.10	53.25	15.65	31.08
Diethylamine	65.61	15.20	19.12	65.66	15.17	19.15
Triethylamine	71.25	15.02	13.79	71.20	14.95	13.84
Butylamine	65.59	15.43	19.10	65.66	15.17	19.15
Dibutylamine	74.17	14.95	11.09	74.32	14.82	10.83
Tributylamine	77.75	14.71	7.62	77.74	14.69	7.55
Isopropylamine	60.83	15.40	23.47	60.94	15.35	23.71
sec-Butylamine	65.56	15.19	19.08	65.66	15.17	19.15
Cyclohexylamine	72.52	13.28	14.14	72.65	13.22	14.12

TABLE 5

Boiling Points of the Amines Isolated and Analytical Data for their Chloroplatinates

Amine	Boiling point of amine			Platinum content of chloroplatinate (%)	
	Found in °C (p in mm Hg)	Reported in literature in °C (p in mm Hg)	Literature reference	found	calculated
Diethylamine	55-56 (756)	55-56 (767.8)	[20]	35.01	35.09
Triethylamine	88-89 (756)	89-89.5 (736.5)	[21]	31.79	31.88
Butylamine	76-77 (756)	77.8 (760.4)	[22]	35.11	35.09
Dibutylamine	159 (756)	159 (761)	[22]	29.25	29.21
Tributylamine	215-216 (753)	216.5	[22]	25.10	25.01
Isopropylamine	33-35 (748)	33-34	[23]	36.81	36.96
sec-Butylamine	61-63 (750)	63 (750)	[24]	31.97	35.09
Cyclohexylamine	133-135 (755)	133-134	[25]	32.11	32.09

From 24 g of the condensate from the reductive amination of butyraldehyde over active charcoal the following fractions were isolated by the method indicated above:

Fraction I	B. p.	85-214° (752 mm);	0.2 g
Fraction II	B. p.	214-219° (752 mm);	1.5 g
Residue			11.5 g

The elementary analysis of Fraction II was (%): C 77.80; H 14.61; N 7.78.

On the basis of these results Fraction II corresponds to tributylamine.

The results on the catalytic synthesis of amines obtained from the amination condensates of cyclohexanol [26] and of the ketones used in these experiments [6] have been described previously. It was established that in the catalytic amination of aliphatic alcohols, not only amines, but also nitriles, aldehydes, ketones, saturated and unsaturated hydrocarbons, hydrogen, and water were formed.

The catalyzates obtained by the amination of etherswere not investigated in detail on account of their low amine contents.

DISCUSSION OF RESULTS

The experiments on the amination of alcohols have established that amines are formed in considerable amounts in presence of platinized silica gel or active charcoal.

It is impossible to imagine, however, that alcohols could form intermediate compounds with these catalysts. It must be considered that Sabatier and Maihle's ideas relating to the formation of an intermediate compound between the alcohol and the catalyst in the course of the amination do not apply in these cases.

Baum's proposed reaction scheme for the amination of alcohols is also not supported by our investigations. The experiments showed that ethers gave much lower yields of amines than alcohols did. This is true for catalysts other than those used by us: in his dissertation Baum gives tables in which it is shown that in presence of alumina, butyl alcohol treated with ammonia at 450° at a molar ratio of ammonia to alcohol of three gives 39.5% of amines. On the other hand, dibutyl ether, at the same ratio of ammonia to ether, yields 32.8% of amines at 300°, and is decomposed completely at 450° with formation of an olefin and water. A further defect of this scheme is that it is in conflict with the fact that tertiary amines are formed. Here Baum is forced to abandon his scheme and refer to some "usual way" in which the tertiary amines are considered to be formed.

With regard to Mignonac's scheme for the explanation of the formation of amines from alcohols via the intermediate stage of carbonyl compounds, in order to resolve the question of its validity it is sufficient to compare our amination results for alcohols with those for the corresponding aldehydes and ketones. The experiments have shown that there is a considerable difference, both in the total yield of amines, and also in the relative amounts of primary, secondary, and tertiary amines. It may be pointed out here that primary alcohols give much higher yields of amines than the corresponding aldehydes do, irrespective of the catalyst used. This is a result of the far-reaching changes and resinification undergone by aldehydes and aldehyde-ammonias under the conditions of the experiments. It is only in the presence of active charcoal that secondary alcohols are aminated more readily than the corresponding ketones; on platinized silica gel these alcohols give lower yields of amines than the ketones do. Only in one case, the amination of cyclohexanol and cyclohexanone over active charcoal, were identical yields of amine (cyclohexylamine)obtained. Hence, with rare exceptions, it is impossible to regard aldehydes and ketones as intermediates in the amination of alcohols.

The results of our experiments give us reason to maintain that the process of the amination of alcohols consists in the simple elimination of the elements of water from the alcohol and ammonia at the catayst surface without the formation of intermediate compounds. By the same dehydration process the primary amine yields a secondary amine, and the secondary a tertiary. However, the rates of these dehydration reactions occurring simultaneously between the alcohol and ammonia, primary amine, and secondary amine are different. The relative amounts of the various amines formed will therefore be different.

Also, the dehydration reaction may be confined to the alcohol molecule, so that unsaturated hydrocarbons will be formed. It is known that water is particularly readily eliminated from tertiary alcohols, and these therefore form mainly unsaturated hydrocarbons, and not amines. Aldehydes and ketones arise under amination conditions as a result of the dehydrogenation of alcohols. When these carbonyl compounds react with ammonia and hydrogen, amines may again be formed, though in insignificant amount. In particular cases, in the amination of certain secondary alcohols, there is no reason to reject this method of amine formation. It occurs when the ketone formed can undergo amination at temperatures of the order of 350° and higher.

SUMMARY

1. The view that alcohols are converted into amines with intermediate formation of aldehydes, ketones, ethers, or unstable compounds between the alcohol and the catalyst is not supported by experiment.

2. In the catalytic amination of alcohols, amines are formed by the direct elimination of the elements of water from molecules of alcohol and ammonia or alcohol and amine, when these come together at the catalyst surface.

LITERATURE CITED

[1] P. Sabatier, Catalysis in Organic Chemistry, State Chem. Press, Leningrad, 1932.

[2] E. K. Smolensky, Roczni i Chemji 1, 232 (1921); G. W. Dorrel, J. Chem. Soc. 127, 2399 (1925).

[3] N. I. Shuikin, A. A. Balandin, and Z. I. Platnik, J. Gen. Chem., 4, 1444 (1934).

[4] E. D. Schwegler, H. Adkins, J. Am. Chem. Soc. 61, 3499 (1939).

[5] L. Baum, Über d. katalyt. Alkylierung v. Ammoniack, Zurich, 1945.

[6] M. A. Popov, J. Gen. Chem., 18, 1109 (1948); M. A. Popov and N. I. Shuikin, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1951, No. 2, 140; M. A. Popov, N. I. Shuikin, and O. L. Baranovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, No. 1, 91.*

[7] M. A. Popov, J. Gen. Chem., 18, 438 (1948).

[8] V. Luginin, Ann. Chim. Phys. (7), 13, 330 (1898).

[9] D. I. Mendeleev, Ann. Phys. 138, 230 (1896).

[10] H. Jahn, Ann. d. Phys. u. Chem., N. F. 43, 301 (1891).

[11] J. W. Brühl, Ann. 203, 1 (1880).

[12] I. Heilbron, Dictionary of Organic Compounds, 1, 4, Moscow, Foreign Lit. Press, 1949.

[13] J. W. Brühl, Ann. 203, 18 (1880).

[14] H. Loomis, Z. Phys. Chem. 32, 601 (1900).

[15] A. Lieben, A. Rossi, Ann. 158, 168 (1871).

[16] G. Schroter, , W. Sonday, Ber. 41, 1922 (1908).

[17] W. H. Perkin, J. pr. Chem. (2), 31, 513 (1885).

[18] F. C. Weber, J. B. Wilson, J. Biol. Chem. 35, 385 (1918).

[19] M. Francois, Comptes rend. 144, 567, 857 (1907).

[20] A. W. Hofmann, Ber 22, 705 (1889).

[21] J. W. Brühl, Ann. 200, 186 (1880).

[22] A. Berg, Ann. Chim. Phys. (7), 3, 294 (1894).

[23] N. A. Menshutkin, J. Russ. Chem. Soc., 29, 453 (1897).

[24] A. Mailhe, Comptes rend. 141, 114(1905).

[25] Yu. K. Yuryev and I. K. Korobitsyna, Bull. Moscow State Univ., 3, 87 (1950).

[26] M. A. Popov and N. I. Shuikin, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1950, No. 4, 370.

---

* Consultant's Bureau Translation, p. 81

Received March 16, 1954

N. D. Zelinsky Institute of Organic
Chemistry of the USSR Academy of
Sciences

BLANK
PAGE

REACTIONS OF INDIVIDUAL HYDROCARBONS IN CONTACT WITH NATURAL ALUMINOSILICATES

COMMUNICATION 3. REACTIONS OF CYCLOPENTANE, ETHYLCYCLOPENTANE, ETHYLCYCLOHEXANE, AND ETHYLBENZENE IN PRESENCE OF TROSHKOV CLAY

N. I. Shuikin and E. A. Timofeeva

In our preceding communication [1] we have given the results of an investigation of the behavior of cyclohexane, methylcyclohexane, and toluene in contact with Troshkov clay. The behavior of the two cycloalkanes indicates that the higher the molecular weight of the cycloalkane, the greater the extent of its conversion into other products. This work shows also that, under the conditions of the catalysis, alkylation, which proceeds simultaneously with dehydrogenation of the cycloalkanes, is the predominant reaction.

The present paper describes a study of the reactions of two five-membered cycloalkanes – cyclopentane and ethylcyclopentane – and also of ethylcyclohexane and ethylbenzene. In the main, the results confirm the regularities observed in the previous investigation.

EXPERIMENTAL

Cyclopentane was prepared by depolymerization of the dimer of cyclopentadiene in a continuous apparatus [2], followed by hydrogenation of the resulting cyclopentadiene in presence of finely dispersed nickel carried by aluminum. Ethylcyclopentane was synthesized from adipic acid via cyclopentanone, 1-ethylcyclopentanol, and 1-ethylcyclopentene. Ethylcyclohexane was prepared by the catalytic hydrogenation of ethylbenzene in presence of a nickel catalyst and hydrogen under pressure. The hydrocarbons prepared in this way were distilled through a 70-plate column. They had the following properties:

	B.p. in °C (corr.)	n_D^{20}	d_4^{20}
Cyclopentane	48.5-49.5	1.4070	0.7462
Ethylcyclopentane	103.2-103.4	1.4190	0.7664
Ethylcyclohexane	131.0	1.4335	0.7878
Ethylbenzene	136.0	1.4960	0.8670

All experiments were carried out in the usual continuous-flow apparatus at 500° and atmospheric pressure, and the same portion of catalyst was used throughout (volume 100 ml, weight 93.1 g, length of layer 43.5 cm, internal diameter of catalysis tube 20 mm). The Troshkov (Siberian) clay was activated with sulfuric acid. Its chemical composition is given in one of our papers [3]. When the experiments on a given hydrocarbon had been completed, the catalyst was regenerated by oxidation with air at 500° for 4-5 hours.

Reactions of Cyclopentane

Cyclopentane was passed in 25 ml (18.6 g) portions at a space velocity of 0.15. The results of the experiments are summarized in Table 1.

The results obtained when the united catalyzate from all experiments (41.8 g) was distilled through a 70-plate column are given in Table 2.

Fraction I was treated with 82% sulfuric acid in order to remove unsaturated hydrocarbons. After being washed with water and dried over calcium chloride, this fraction came over in the range 34.2-49.0° (752 mm) when distilled over sodium, and it had n_D^{20} 1.3960; d_4^{20} 0.7325, and aniline point 21.2° (in a sealed tube). The high aniline point (the aniline point of cyclopentane is 18°) indicates that this fraction contained not only unchanged cyclopentane and C_5 unsaturated hydrocarbons, but also n-pentane. Fraction II was practically

BLANK
PAGE

naphthene-paraffin part was completely free of aromatics (negative formolite test) and unsaturated hydrocarbons (Bayer test). The fractionation curves for the two parts of the catalyzate are shown in Figures 1 and 2.

TABLE 3

Properties of Ethylcyclopentane Catalyzates

Expt. no.	Yield of catalyzate (%)	Yield of gas (liter, NTP)	Properties of Catalyzate				
			n_D^{26}	d_4^{26}	Content of sulfonatable hydrocarbons (% by volume)	Iodine number	Content of unsaturated hydrocarbons (% by weight)
1	96.1	4,153	1.4280	–	22.0	–	–
2	95.0	4,831	1.4310	–	–	–	–
3	93.0	5,325	1.4280	0.7730	22.0	11.6	4.6
4	93.0	5,133	1.4320	–	–	–	–
5	94.0	5,286	1.4320	0.7746	25.0	12.0	4.7
6	92.0	5,066	1.4310	–	–	–	–
7	96.1	4.914	1.4296	0.7752	23.0	10.6	4.1
8	93.0	5,996	1.4325	–	–	–	–

TABLE 4

Properties of Fractions of the United Ethylcyclopentane Catalyzate

Fraction no.	Boiling range (°C corr.)	Amount (g)	n_D^{20}	d_4^{20}	Iodine number	Aniline point
			From the naphthene-paraffin part			
I	68.2–92.6	3.6	1.4035	0.7281	–	50.5
II	92.6–102.9	8.5	1.4160	0.7618	–	40.5
III	102.9–103.3	134.0	1.4136	0.7640	–	–
Residue		0.3	1.4200	–	–	–
			From the aromatic part (together with unsaturated hydrocarbons)			
IV	57.9–78.9	1.1	1.4130	0.7198	266.5	–
V	78.9–102.3	1.9	1.4300	0.7466	184.9	–
VI	102.3–115.0	22.9	1.4860	0.8523	23.7	–
VII	115.0–200.0	13.2	1.5240	0.9062	0.9	–
Residue		0.4	1.5280	–	–	–

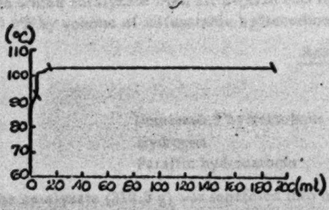


Fig. 1. Fractionation curve of the naphthene-paraffin part of the ethylcylcopentene catalyzate.

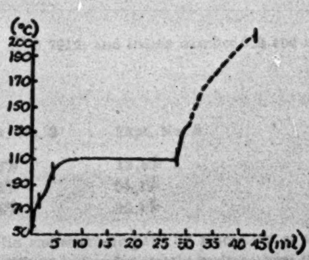


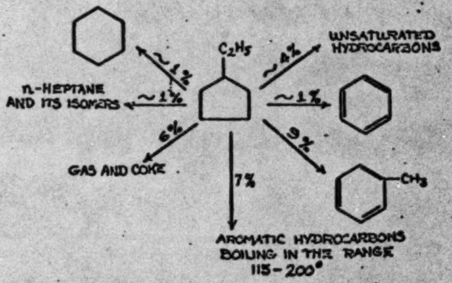
Fig. 2. Fractionation curve of aromatic part (together with unsaturated hydrocarbons) of the ethylcyclopentane catalyzate

Fraction I of the naphthene-paraffin part of the catalyzate was submitted to exhaustive dehydrogenational catalysis. Its refractive index was then raised from 1.4035 to 1.4310. After removal of the benzene formed, the fraction had n_D^{20} 1,3850, d_4^{20} 0.6798, and an aniline point of 70°. Fraction I, therefore, contained cyclohexane and, judging from the properties of the dearomatized catalyzate, also heptane isomers. The rather high aniline point (40.5°) of Fraction II (92.6–102.9°), as compared with the aniline point of pure ethylcyclopentane (38.7°), indicates that it contained some heptane isomers. Fraction III (102.9–103.3°) was almost pure unchanged ethylcyclopentane.

Fraction IV of the aromatic part of the catalyzate had an iodine number of 266.5 and consisted mainly of unsaturated hydrocarbons; it is possible, however, that this small fraction contained a little benzene. Fraction V, judging by its properties, boiling range, and high iodine number, contained an appreciable amount of C_7 unsaturated hydrocarbons, and the value of the iodine number indicates that the content of unsaturated hydrocarbons was about 70%, the remainder being apparently benzene. The properties of Fraction VI show (see also the fractionation curve) that it was mainly toluene, but the iodine number indicates that it contained also about 10% of C_8 unsaturated hydrocarbons. Fraction VIII contained a little toluene, but consisted mainly of xylenes and higher benzene homologs (see fractionation curve).

Hence, as a result of the passage of ethylcyclopentane in contact with activated Troshkov clay under the given conditions, 22% of sulfonatables was obtained, and this consisted mainly of aromatic hydrocarbons, since the iodine number of the united catalyzate was only 11.4. These consisted mainly of toluene (9%), formed, no doubt, as a result of the isomerization of ethylcyclopentane to methylcyclohexane and the dehydrogenation of the latter. The yield of benzene and its higher homologs amounted to about 7%, calculated on the original hydrocarbon. In addition, cleavage of the five-membered ring occurred, with formation of about 1% of n-heptane and its isomers.

The observed reactions of ethylcyclopentane can be represented by the following scheme:



C_2H_5
~1%
UNSATURATED HYDROCARBONS
~4%
n-HEPTANE AND ITS ISOMERS
~1%
~1%
6%
GAS AND COKE
9%
7%
CH_3
AROMATIC HYDROCARBONS BOILING IN THE RANGE 115-200°

The degree of conversion was 26-28%.

Reactions of Ethylcyclohexane

Ethylcyclohexane was passed over the same catalyst, after regeneration, in 50 ml (39.4 g) portions at a space velocity of 0.3. Altogether, 450 ml (354.5 g) of hydrocarbon was passed. The properties of the resulting catalyzates are given in Table 5.

The united catalyzate from all experiments had n_D^{20} 1.4450; d_4^{20} 0.7912; and iodine number 0.9, and it contained 30.0% by volume of sulfonatable hydrocarbons.

Analysis of gas

	Expt. No. 3	Expt. No. 8
Unsaturated hydrocarbons	12.3%	12.8%
Hydrogen	58.1%	54.1%
Paraffin hydrocarbons	29.6%	33.1%

The catalyzate (312.5 g) was separated into naphthene-paraffin and aromatic parts by adsorption on silica gel. The naphthene-paraffin part of the catalyzate was quite free from unsaturated and aromatic hydrocarbons (negative Bayer and formolite tests). The fractionation curves for the two parts of the catalyzate are given in Figures 3 and 4.

The properties of the fractions so obtained are given in Table 6. The naphthene-paraffin part of the catalyzate was fractionated through a 70-plate column, and the aromatic part — through a 20-plate column.

TABLE 5

Properties of Ethylcyclohexane Catalyzates

Expt. no.	Yield of catalyzate (%)	Yield of gas (liter, NTP)	Properties of catalyzate			
			n_D^{20}	d_4^{20}	Content of sulfonatable hydrocarbons (% by volume)	Iodine number
1	80.5	6.758	1.4430	0.7906	30.0	0.7
2	84.9	7.280	1.4430	–	–	–
3	85.3	7.528	1.4460	0.7951	30.0	1.0
4	86.0	7.282	1.4425	–	–	–
5	86.0	7.368	1.4420	0.7908	27.0	0.9
6	85.9	7.565	1.4460	–	–	–
7	85.3	7.397	1.4450	0.7909	–	0.9
8	86.0	7.960	1.4450	–	–	–
9	86.0	7.538	1.4460	–	32.0	–

TABLE 6

Properties of Fractions of the Ethylcyclohexane Catalyzate

Fraction no.	Boiling range (°C corr.)	Amount (g)	n_D^{20}	d_4^{20}	Iodine number	Aniline point
			From the naphthene-paraffin part			
I	47.8 – 81.8	4.2	1.3910	0.7018	–	70.8
II	81.8 – 130.1	25.3	1.4260	0.7755	–	46.8
III	130.1 – 131.0	185.0	1.4325	0.7865	–	44.0
Residue		0.4	1.4395	–	–	–
			From the aromatic part			
IV	58.8 – 78.3	1.7	1.4245	0.7731	62.1	–
V	78.3 – 83.1	2.3	1.4500	–	54.0	–
VI	83.1 – 122.5	15.7	1.4910	0.8568	4.2	–
VII	122.5 – 140.0	21.5	1.4900	0.8596	0.0	–
VIII	140.0 – 147.0	32.5	1.4920	0.8660	7.3	–
IX	147.0 – 210.0	11.4	1.5061	0.8787	11.5	–
Residue		0.5	1.5130	–	–	–

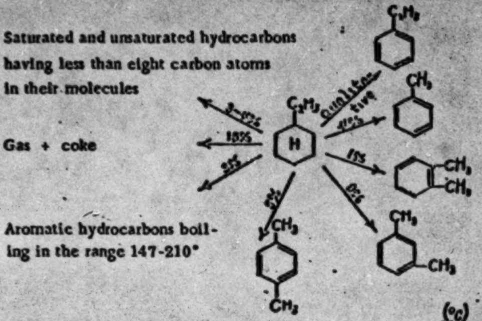
Fraction I, judging from its properties, consisted of alkanes. Investigation of Fractions II and III by the Raman-spectrum method indicated that they consisted mainly of unchanged ethylcyclohexane. The properties of Fraction II, however, indicated that it contained also a small amount of alkanes.

The compositions of the fractions obtained from the aromatic part of the catalyzate were determined by the Raman-spectrum method. It was found that Fractions IV and V consisted of a mixture of unsaturated hydrocarbons and benzene. Fraction VI contained a considerable amount of toluene and traces of unsaturated hydrocarbons. Fractions VII and VIII consisted of m-xylene (about 60%), p-xylene (about 27%), o-xylene (about 6%), and a little ethylbenzene. Fraction IX contained higher benzene homologs boiling over the range 147-210°, in admixture with unsaturated hydrocarbons.

Hence, the main reactions of ethylcyclohexane in contact with activated Trochkov clay consisted in the formation of aromatic hydrocarbons, namely, toluene, isomeric xylenes, ethylbenzene, and higher benzene homologs boiling in the range 147-210°; at the same time a small amount of alkanes was formed.

The contact-catalysis reactions of ethylcyclohexane under the given conditions may be represented schematically as follows: (see top of following page).

The degree of conversion was 40-41%.


Saturated and unsaturated hydrocarbons having less than eight carbon atoms in their molecules
Gas + coke
Aromatic hydrocarbons boiling in the range 147-210°
C2H5
H
C2H5
CH3
CH3
CH3
CH3
CH3
CH3
CH3
3-12%
15%
9%
quantitative
41%
15%
0.6%
6%

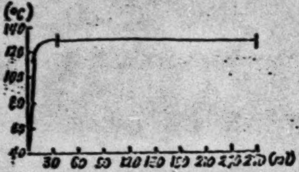


Fig. 3. Fractionation curve of the naphthene-paraffin part of the ethylcyclohexane

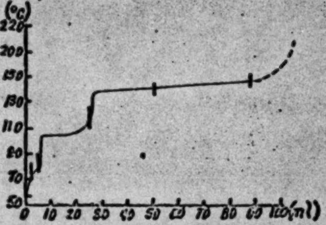


Fig. 4. Fractionation curve of the aromatic part (together with unsaturated hydrocarbons) of the ethylcyclohexane catalyzate.

Table 7 gives the values of the degrees of conversion of the cycloalkanes that we have studied, and it gives also the yields of aromatic hydrocarbons formed from the cycloalkanes in the catalytic treatment.

TABLE 7

Reactions of Cycloalkanes in Contact with Activated Troshkov Clay

Hydrocarbon	Degree of conversion (% by weight on original hydrocarbon)	Amount of aromatics (% on original hydrocarbon)
Cyclopentane	10-12	1
Cyclohexane	11-12	3
Ethylcyclopentane	26-28	17
Methylcyclohexane	30-32	11
Ethylcyclohexane	40-41	22

It will be seen from Table 7 that the degree of the conversion of the cycloalkane and the yield of aromatic hydrocarbons rise as the molecular weight rises.

Contact-catalysis Reactions of Ethylbenzene

Ethylbenzene was passed in 50-ml (43.4-g) portions. The properties of the ethylbenzene catalyzates are given in Table 8.

Analysis of gas

Unsaturated hydrocarbons	9.8%
Hydrogen	82.8%
Paraffin hydrocarbons	7.4%

The fractionation curve for the combined catalyzate from the two experiments fractionated through a 20-plate column is given in Fig. 5. For the fractionation 70.0 g of catalyzate was taken. The yields and properties of the fractions of the catalyzate are given in Table 9.

TABLE 8

Properties of Ethylbenzene Catalyzates

Expt. no.	Yield of catalyzate (%)	Yield of gas (liter, NTP)	Properties of catalyzate			
			n_D^{20}	d_4^{20}	Content of sulfonatable hydrocarbons (% by volume)	Iodine number
1	94.0	1.528	1.4977	0.8700	98.0	2.8
2	95.0	1.435	1.4975			

TABLE 9

Properties of Fractions of the United Ethylbenzene Catalyzate

Fraction no.	Boiling range (°C)	Yield		Properties of the fraction			
		(g)	(% by weight)	n_D^{20}	d_4^{20}	Bayer test	Iodine number
I	78.1–83.1	3.0	4.3	1.4983	0.8756	Negative	–
II	83.1–136.0	61.7	89.3	1.4960	0.8666	Negative	–
III	136.0–200	4.0	5.7	1.5215	0.9030	Positive	27.5
Residue		0.4	0.6	1.5300	–	–	–

It will be seen from Table 9 and the fractionation curve that, under the given conditions, ethylbenzene yielded 4.3% of benzene (Fraction I) and 5.8% of higher aromatic hydrocarbons admixed with a small amount of unsaturated hydrocarbons (Fraction III). Fraction II consisted mainly of unchanged ethylbenzene admixed with very small amounts of benzene. Thus, ethylbenzene, like toluene, was very stable under the catalytic treatment: 89% of it remained unchanged.

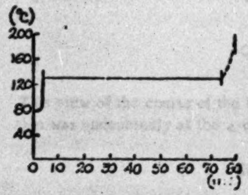


Fig. 5. Fractionation curve of the ethylbenzene catalyzate.

If the dehydrogenation of ethylcyclohexane had occurred more rapidly than the synthesis from it of new alkyl-substituted cyclohexanes (mainly methyl derivatives), then the catalyzate would have consisted mainly of ethylbenzene. Actually, however, ethylbenzene was detected only qualitatively in the ethylcyclohexane catalyzate. Hence, under the given conditions, the synthesis of new alkyl-substituted cyclohexanes was more rapid than the dehydrogenation of the original ethylcyclohexane.

SUMMARY

1. A study has been made of the reactions of cyclopentane, ethylcyclopentane, ethylcyclohexane, and ethylbenzene in contact with activated Troshkov clay at 500°.

2. It has been established that the degree of conversion of cycloalkanes increases with increase in molecular weight. For cyclopentane the degree of conversion is 10-12%, for ethylcyclopentane it is 26-28%, and for ethylcyclohexane it is 40-41%.

3. On the basis of a comparative study of the behavior of ethylcyclohexane and ethylbenzene it is suggested that under the given catalysis conditions, reactions leading to the synthesis of alkyl derivatives are more rapid than the dehydrogenation of the original ethylcyclohexane.

LITERATURE CITED

[1] E. A. Timofeeva and N. I. Shuikin, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 6, 1075 (1954).

[2] N. F. Kononov, Z. Ya. Lapshina, and S. S. Novikov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 112 (1953).*

[3] N. I. Shuikin and E. A. Timofeeva, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 6, 828 (1951).

Received April 14, 1954.

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

---

* Consultants Bureau Translation, p. 101.

BLANK
PAGE

PHOTODEHYDROCONDENSATION OF ANISOLE HOMOLOGS.

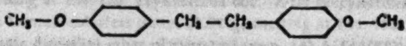
PHOTOSYNTHESIS OF SYNESTROL

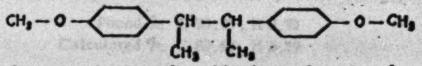
B. M. Mikhailov and A. N. Blokhina

Under the influence of sunlight benzene homologs react with ketones with formation of compounds of two types, alcohols and hydrocarbons. Thus, by prolonged insolation of a mixture of toluene and benzophenone, Ciamician and Silber [1] have obtained bibenzyl and 1,1,2-triphenylethanol. When irradiated, ethylbenzene and benzophenone gave a hydrocarbon and an alcohol, and also benzopinacol [2]. The structures of the hydrocarbon and the alcohol were not established, but the composition of the hydrocarbon ($C_{16}H_{18}$) suggests that it could be 1,4- or 2,3-diphenylbutane. Other benzene homologs (p-propybenzene and p-xylene) give similar reactions.

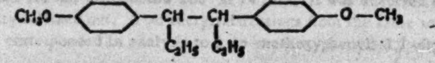
We have investigated the photochemical reactions of anisole homologs in presence of acetone, the mixture of reactants being exposed to ultraviolet radiation and we have found that, under these conditions, para homologs of anisole undergo photodehydrocondensation reactions and yield methoxyphenyl derivatives of aliphatic hydrocarbons.

p-Methylanisole yielded 4,4'-dimethoxybibenzyl (I). p-Ethylanisole underwent condensation at its α-carbon atoms and yielded 4,4'-dimethyoxy-α,α'-dimethylbibenzyl (II):


(I)

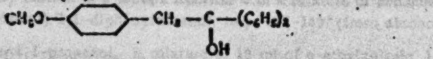

(II)

This view of the course of the latter reaction is confirmed by the condensation of p-propylanisole, in which reaction was undoubtedly at the α-carbons, the product being α,α'-diethyl-4,4'-dimethoxybibenzyl (III):

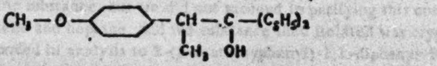

(III)

which was readily hydrolyzed to synestrol (α,α'-diethyl-α,α'-dihydrostilbestrol, or 4,4'-(1,2-diethylethylene), a synthetic female sex hormone of high activity.

When a mixture of p-methylanisole and benzophenone was irradiated in acetone solution, not only 4,4'-dimethoxybibenzyl was formed, but also the product of the condensation of p-methylanisole with benzophenone, 2-(p-methoxyphenyl)-1,1-diphenylethanol (IV):


(IV)

When p-ethylanisole was irradiated under similar conditions, an alcohol was obtained. This product was evidently 2-(p-methoxyphenyl)-1,1-diphenyl-1-propanol (V):


(V)

EXPERIMENTAL

Starting Materials. p-Methylanisole was prepared by the methylation of p-cresol and boiled at 75-77° (22 mm) [3]. p-Ethylanisole, b.p. 112° (46 mm), was prepared by the methylation [3] of p-ethylphenol, which was itself prepared by the reduction [4] of 4'-hydroxyacetophenone [5]. In order to obtain p-propylanisole (b.p. 211-212°), anisole was condensed with propionyl chloride [6], and the resulting 4'-methoxypropionophenone was subjected to Clemmensen reduction [7].

All experiments were carried out in quartz flasks hermetically closed with corks. The air was displaced from the reaction vessels with nitrogen. A PRK-4 quartz lamp was used as a source of ultraviolet radiation. The reaction vessels were placed at a distance of 30 cm from the lamp.

4,4'-Dimethoxybibenzyl. A mixture of 30 ml of p-methylanisole and 40 ml of acetone was irradiated for 230 hours. Acetone and p-methylanisole were distilled off, and the oily reside (1.45 g) partially crystallized when treated with ethanol. The substance obtained (0.09 g) was crystallized from ethanol and formed long colorless plates, m.p. 129-130°. The reported melting point of 4,4'-dimethoxybibenzyl is 128.5-130° [8].

Found %: C 79.60; H 7.62

$C_{16}H_{18}O_2$. Calculated %: C 79.29; H 7.49

4,4'-Dimethoxy-α.α'-dimethylbibenzyl. A mixture of 20 ml of p-ethylanisole and 35 ml of acetone was irradiated for 200 hours. After removal of acetone at atmospheric pressure and p-ethylanisole at 6 mm Hg, 1.56 g of an oily residue was obtained. Treatment of this with methanol yielded a crystalline substance (0.08 g), which after crystallization from the same solvent melted at 136-136.5° and which corresponded in analysis to 4,4'-dimethoxy-α.α'-dimethylbibenzyl.

Found %: C 79.83 H 8.31

$C_{18}H_{22}O_2$ Calculated %: C 79.95 H 8.20

α.α'-Diethyl-4,4'-dimethoxybibenzyl (Dimethyl Ether of Synestrol). A mixture of 20 ml of p-propylanisole and 35 ml of acetone was irradiated for 235 hours. Acetone was then driven off from a water bath. and the unchanged p-propylanisole was distilled off under reduced pressure. The oily residue (1.34 g) was dissolved in methanol., and 0.04 g of a substance melting at 124-130° crystallized out. After recrystallization from a mixture of acetone and methanol, the substance formed colorless plates (0.02 g) melting at 144-145°. The melting point was not depressed by admixture of synthetic dimethyl ether of synestrol (m.p. 143.5-144° [9]).

Found %: C 80.67; H 8.75

$C_{20}H_{26}O_2$ Calculated %: C 80.48; H 8.79

2-(p-Methoxyphenyl)-1,1,-diphenylethanol. A mixture of 10 ml of p-methylanisole, 15 g of benzophenone, and 15 ml of acetone was irradiated for 240 hours. Unchanged starting materials were removed by distillation, and a residue of 2 g remained which did not distil below 185° at 14 mm. It was dissolved in ethanol, and 0.81 g of a substance melting at 129-137° crystallized out. Two recrystallizations from the same solvent yielded needles melting at 141-142.5° The substance corresponded in analysis to 2-(p-methoxyphenyl)-1,1-diphenylethanol.

Found %: C 82.94; H 6.72

$C_{21}H_{20}O_2$ Calculated %: C 82.85; H 6.62

The main mother liquor was evaporated down, and the residue was dissolved in a mixture of benzene and n-hexane (1 : 1) and subjected to chromatographic analysis on alumina (20 g). The first fraction (150 ml) contained a substance which, after crystallization from alcohol, had a melting point of 129-130°, undepressed by admixture of a sample of 4,4'-dimethoxybibenzyl. By elution of a second fraction with a mixture of benzene and alcohol (1 : 1), a further 0.43 g of 2-(p-methoxyphenyl)-1,1-diphenylethanol, m.p. 137-140° (from alcohol) was isolated.

2-(p-Methoxyphenyl)-1,1-diphenyl-1-propanol. A mixture of 10 ml of p-ethylanisole, 13 g of benzophenone, and 20 ml of acetone was irradiated for 110 hours. The residue (5 g) obtained after removal of unchanged starting materials was dissolved in a mixture of benzene and n-heptane (1 : 6) and subjected to chromatographic analysis on alumina. At first, elution was effected with a mixture of the same solvents in the same proportions. The first fraction (250 ml) contained a crystalline substance, but we did not succeed in purifying this completely. Elution was continued with a 1 : 1 mixture of benzene and heptane, and the substance then isolated was crystallized from alcohol. It melted at 107-108°, and corresponded in analysis to 2-(p-methoxyphenyl)-1,1-diphenyl-1-propanol.

Found %: C [illegible]; H 6.92

$C_{22}H_{22}O_2$ Calculated %: C 82.97; H 6.96

SUMMARY

1. When exposed to ultraviolet radiation in presence of acetone, para anisole homologs undergo dehydrocondensation with formation of p-methoxyphenyl derivatives of aliphatic hydrocarbons. In particular, synestrol can be obtained by this method from p-propylanisole.

2. When these reactions are carried out in presence of benzophenone, in addition to dehydrocondensation products it is possible to isolate 2-(p-methoxyphenyl)-1,1-diphenyl-1-alkanols, formed by the condensation of the para anisole homologs with the ketone.

Received June 17, 1954

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

LITERATURE CITED

[1] G. Ciamician, P. Silber, Ber. 45, 1536 (1910).

[2] E. Paterno, G. Ghieffi, Gazz. chim. Ital. 39, II, 415 (1909).

[3] H. Hodgson, J. Nixon, J. Chem. Soc. 1930, 2166

[4] E. Clemmensen, Ber. 45, 53 (1914).

[5] Syntheses of Organic Substances, 2, 426.

[6] A. Klages, Ber. 35, 2262 (1902).

[7] B. Jonson, W. Hodge, J. Am. Chem. Soc. 35, 1014 (1913).

[8] An. Sosa, Ann. Chim. 145, 120 (1940).

[9] A. Wilds, W. McCormack, J. org. Chem. 14, 45 (1949).

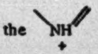
BLANK
PAGE

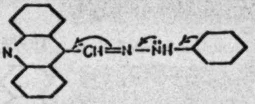
ABSORPTION SPECTRA AND MOLECULAR STRUCTURE*

COMMUNICATION 3. MODERN ELECTRONIC THEORY, AND THE COLOR OF ARYLHYDRAZONES OF 9-ACRIDINECARBOXALDEHYDE

A. A. Kharkharov

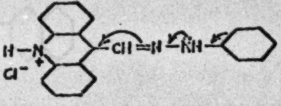
An open discussion on problems of chemical structure has revealed that the concept of resonance is scientifically unsound, and it has directed the work of Soviet chemists along the lines of the further evolution of the teaching of Butlerov and Markovnikov. It has shown the great significance, as a modern interpretation of teaching relating to the mutual effects of atoms and groups of atoms, of the electronic theory that is being developed in organic chemistry by Soviet investigators.

For the experimental verification of hypotheses based on electronic theory in its application to the color of organic compounds, we have used data derived from spectrum investigations of arylhydrazones of 9-acridinecarboxaldehyde [1]. Hydrochlorides of 9-acridinecarboxaldehyde arylhydrazones behave as typical dyes; not only are they deeply and intensely colored, but they are able to dye textile fibers. The powerful bathochromic effect that we observe as we pass from the hydrazone bases to their salts is to be explained by the enhanced electron-accepting properties of the acridine nitrogen, due to the addition of a proton at its free electron pair, and the consequent marked change in the positions of all energy levels of the molecule. The effect of the  group extends over the whole molecule. Raising of the ground-state energy level of the molecule is accompanied by a deepening of color, for it is usually found that, when the energy levels are higher, they are closer together. The higher the ground state of a molecule, the less is the change in energy in an electron transition from the ground state to an excited state. This effect can be seen when we compare the color of 9-acridinecarboxaldehyde phenylhydrazone (λ_{max} 465 mμ) (Fig. 1.):



(Yellow)

with that of its hydrochloride (λ_{max} 562 mμ) (Fig. 1):



(Reddish violet)

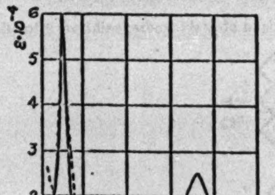
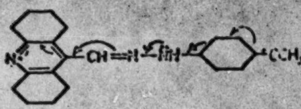


Fig. 1. Absorption spectra of 9-acridinecarboxaldehyde phenylhydrazone: ——— dissolved in alcoholic hydrogen chloride; – – – dissolved in alcohol.

The difference in the positions of the maxima of the principal absorption bands is still greater for 9-acridinecarboxaldehyde p-methoxyphenylhydrazone (λ_{max} 470 mμ):

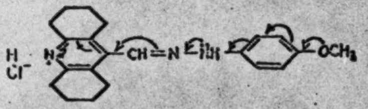
---

*Work performed in fulfilment of requirements for the doctorate of the Institute of Organic Chemistry of the USSR Academy of Sciences.



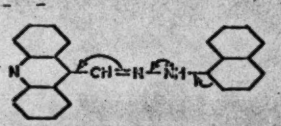
(Yellowish brown)

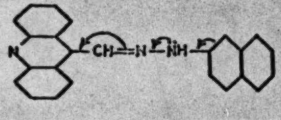
and its salt (λ_{max} 610 mμ):



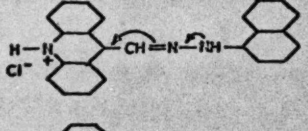
(Greenish blue)

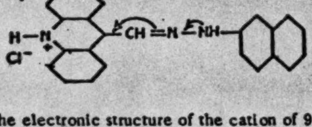
and also for the bases:



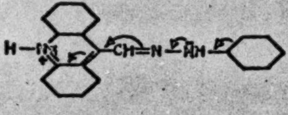


and salts of 9-acridinecarboxaldehyde naphthylhydrazones (Fig. 2 and 3):





On the basis of an examination of the electronic structure of the cation of 9-acridinecarboxaldehyde phenylhydrazone:



we suggested, and confirmed experimentally, that the introduction of electron-donating substituents, such as an acetamido group para to the positively charged nitrogen of the acridine ring system, would result in partial neutralization of this charge. The resulting weakening of the electron-accepting power of the nitrogen is accompanied by a reduction in the diplacement of electrons from the phenyl nucleus to the heterocycle , and so by a shift in the principal absorption maximum towards the short waves. Thus, as we pass from the hydrochloride of

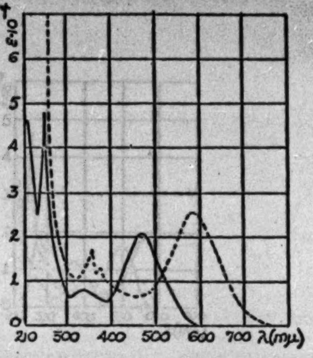


Fig. 2. Absorption spectra of 9-acridinecarboxaldehyde 1-naphthylhydrazone: – – – dissolved in alcoholic hydrogen chloride; ———— dissolved in alcohol.

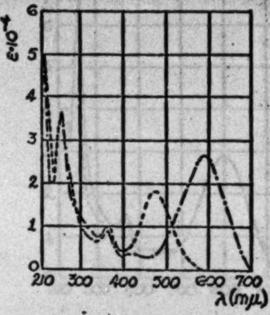
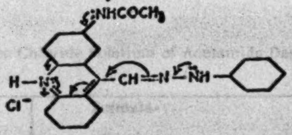
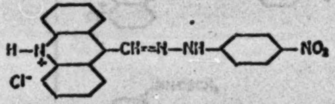


Fig. 3. Absorption spectra of 9-acridinecarboxaldehyde 2-naphthylhydrazone: – · – · –, dissolved in alcoholic hydrogen chloride; – – – dissolved in alcohol.

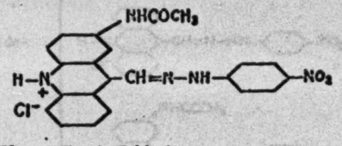
9-acridinecarboxaldehyde phenylhydrazone to the hydrochloride of 2-acetamido-9-acridinecarboxaldehyde:



the principal maximum is displaced from 562 to 512 mμ (Fig. 4, Table 1), and as we pass from the hydrochloride of 9-acridinecarboxaldehyde p-nitrophenylhydrazone:



to the hydrochloride of 2-acetamido-9-acridinecarboxaldehyde p-nitrophenylhydrazone:



the displacement is from 522 to 375 mμ (Fig. 4, Table 1).

Our investigations have thus shown that one of the postulates of the chromophore theory [2], i.e. that the introduction of auxochromic groups results in a deepening of color, is not always true. In the examples examined the introduction of auxochromic groups does not deepen the color, but lightens it.

The theory of electron displacements have enabled us to predict also that the presence of electron-donating substituents in the phenyl nucleus will act synergically with the positively charged nitrogen in bringing about electron displacements directed through the system from the substituent via the phenyl nucleus and the —NH—

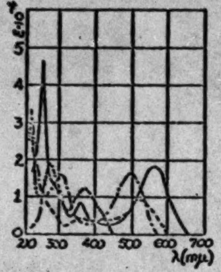


Fig. 4. Absorption spectra in alcoholic hydrogen chloride solutions: 9-acridinecarboxaldehyde phenylhydrazone; — — — 9-acridinecarboxaldehyde p-nitrophenylhydrazone; —·—·—·— 2-acetamido-9-acridinecarboxaldehyde phenylhydrazone; ·········· 2-acetamido-9-acridinecarboxaldehyde p-nitrophenylhydrazone.

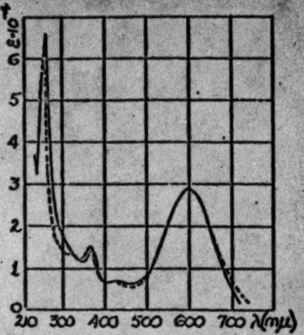
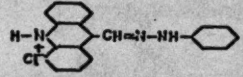
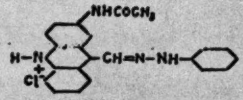
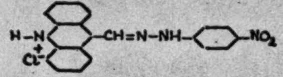
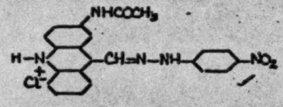
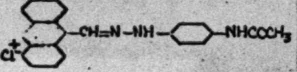


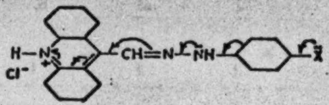
Fig. 5. Absorption spectra of alcoholic hydrogen chloride solutions: — — — 9-acridinecarboxaldehyde p-acetamidophenylhydrazone; ——— 9-acridinecarboxaldehyde p-benzamidophenylhydrazone.

TABLE 1

Absorption Maxima of Alcoholic Hydrogen Chloride Solutions of Acetamido Derivatives of 9-Acridinecarboxaldehyde Phenylhydrazone

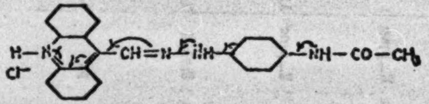
Substance	Formula	Absorption maxima (mμ)		
		1	2	3
Hydrochloride of 9-acridinecarboxaldehyde phenylhydrazone		254	364	562
Hydrochloride of 2-acetamido-9-acridinecarboxaldehyde phenylhydrazone			314	512
Hydrochloride of 9-acridinecarboxaldehyde p-nitrophenylhydrazone		256	364	522
Hydrochloride of 2-acetamido-9-acridinecarboxaldehyde p-nitrophenylhydrazone			278	375
Hydrochloride of 9-acridinecarboxaldehyde p-acetamidophenylhydrazone		256	366	598

group to the nitrogen of the acridine ring system:



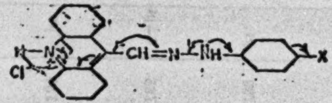
The action of electron-donating substituents is to effect a greater change in the electron densities of all atoms of the system, as compared with the changes in unsubstituted 9-acridinecarboxaldehyde phenylhydrazone, and so to deepen the color.

Thus, if we again introduce the acetamido (or benzamido) group into the unsubstituted compound, i not in position 2 in the acridine ring system, but in the phenyl group e.g. para to the ——NH—— group, there is now a lightening of the color, not deepening, (λ_{max} 598 mμ; Fig. 5, Table 1).



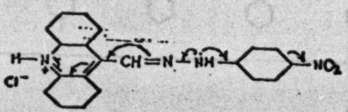
It will be seen that the same substituent, depending on its position in the molecule, may either deepen or lighten the color. This shows that conclusions made on the basis of electronic theory are in accord with experiment, i.e. with practice. All that we have stated concerning auxochromes may be extended also to chromophores.

Electron-accepting groups oppose the tendency of the positively charged nitrogen to attract electrons:



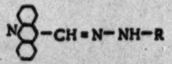
and in this way reduce the disturbances in electron density and lighten the color.

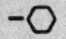
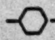
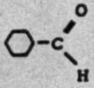
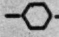
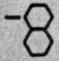
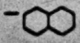
In the present case such electron-accepting substituents as NO_2, CHO, $COCH_3$, which are usually regarded as typical chromophores, do not deepen, but lighten the color. For example, the principal absorption maximum of the hydrochloride of 9-acridinecarboxaldehyde p-nitrophenylhydrazone:

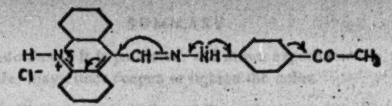


is displaced towards the short waves by 40 mμ, as compared with the unsubstituted compound (Fig. 4, Table 1), and the maximum of the hydrochloride of the p-acetylphenylhydrazone of the same aldehyde:

TABLE 2

Principal Properties of Aryl-hydrazones of 9-acridinecarboxaldehyde  (Abbreviations: y - yellow; g - green; r - red; br - brown; o - orange; v - violet; d - dark)

Compound	R	M.p. (°C)	Color of dry substances		Color of solutions					Principal absorption maximum (mμ)				Color of dyeing on silk
			free	salt	in aqueous alcoholic caustic soda	in alcohol	in alcoholic caustic soda	in concentrated sulfuric acid	in glacial acetic acid	in alcohol	in 0.2 N alcoholic HCl	in aqueous alcoholic caustic soda	in alcoholic caustic soda	
9-Acridinecarboxaldehyde phenylhydrazone		215	br—y	v—black	y	y	y—g	br—y	v—r	400	562	530	640	r—v
9-Acridinecarboxaldehyde p-acetamidophenyl hydrazone	 —NHCOCH$_3$	120	br	g	br	br	br	r—v	blue	—	599	600	—	blue
9-Acridinecarboxaldehyde p-methoxyphenyl hydrazone	—OCH$_3$	182	d—br	d—blue	br—y	br—y	gray-g	y—br	g-blue	470	610	610	—	g—blue
9-Acridinecarboxaldehyde p-formylphenyl hydrazone		138	br	g	o	o	g—blue	y—r	r—v	—	539	540	—	v—r
9-Acridinecarboxaldehyde p-acetylphenyl-hydrazone	—COCH$_3$	201	br	g	y—br	y—br	g—blue	r	v—r	—	540	540	—	v—r
9-Acridinecarboxaldehyde p-nitrophenyl-hydrazone	 —NO$_2$	252	y	g	y	y	blue	o	r	444	522	520	630	blue—r
9-Acridinecarboxaldehyde 1-naphthylhydrazone		195	br	r-black	br	y	br—y	br	blue	467	595	595	—	blue
9-Acridinecarboxaldehyde 2-naphthylhydrazone		207	br	r-black	br	y	g	br	blue	470	592	590	—	blue



is displaced in the same direction by 22 mμ (Fig. 4, Table 1). Hence, not only auxochromes, but also chromophores may, depending on their positions in the molecule, either deepen or lighten the color.

These phenomena, which are predicted by the theory of electron displacements, cannot be explained, and certainly cannot be predicted, either by the chromophore theory [2], by the quinonoid theory [3, 4], or by the coordination theory [5-9].

It should be noted that the quinonoid theory is not only unable to explain the effect of substituents, but is unable also to explain color of 9-acridinecarboxaldehyde phenylhydrazone itself, since its molecule does not have a quinonoid structure. Moreover, Dilthey and Wizinger's theory of coordinative unsaturation is found to be unsound when the effect of the identity and disposition of the substituents is examined. The examples that we have given, therefore, enable us to form a judgement of the greater validity and power of prediction of the theory of electron displacements, as compared with pre-electronic theories of color, including the chromophore theory.

We have now shown, and we shall later illustrate for dyes widely used in practice, that the chromophore theory, which has been borne out by a considerable amount of experimental material and has done great service to chemistry and to the synthetic dye industry is in conflict with practical observations in a number of cases. It is necessary, therefore, to reexamine the chromophore theory from the point of view of electronic theory. In other words, it must be introduced in a more precise form into the theory of electron displacements, so as to form a component part of this theory. The same may be said of the other theories of color. Those postulates of the other theories that are in accord with practice must be taken into account in modern electronic theory. Electronic theory, as applied by us in the establishment of the relation between color and structure in organic compounds, is being developed by many Soviet investigators [10-15].

With the aid of Butlerov's theory of structure, supplemented by electronic theory, "we" as Izmailsky writes [12], "can give an approximate expression of the actual structure with the aid of a single formula, using the conjugation symbol". In Izmailsky's words: electronic formulas are formulas of fine structure - they provide a second degree of approximation to objective reality. Here lies the explanation of the greater cognitive possibilities of electronic theory, as compared with all previous theories.

EXPERIMENTAL

The arylhydrazones of 9-acridinecarboxaldehyde were prepared by the method already described by us [1,15-19]. Their principal properties are given in Table 2. All spectrum investigations were carried out with an SF-1 photoelectric spectrophotometer. Before the measurements were made, the substances were carefully purified, and their purities were checked by analysis (Table 3).

TABLE 3

Analyses of Arylhydrazones of 9-Acridinecarboxaldehyde

Compound	Elementary composition	Molecular weight	Nitrogen content (%)	
			Found	Calculated
9-Acridinecarboxaldehyde phenylhydrazone	$C_{20}H_{15}N_3$	297	14.36	14.14
9-Acridinecarboxaldehyde p-acetamidophenylhydrazone	$C_{22}H_{18}N_4O$	354	15.54	15.82
9-Acridinecarboxaldehyde p-methoxyphenylhydrazone	$C_{21}H_{17}N_3O$	327	12.96	12.84
9-Acridinecarboxaldehyde p-formylphenylhydrazone	$C_{21}H_{15}N_3O$	325	13.25	12.96
9-Acridinecarboxaldehyde p-acetylphenylhydrazone	$C_{22}H_{17}N_3O$	339	12.55	12.39
9-Acridinecarboxaldehyde p-nitrophenylhydrazone	$C_{20}H_{14}N_3O_2$	324	16.34	16.37
9-Acridinecarboxaldehyde 1-naphthylhydrazone	$C_{24}H_{17}N_3$	347	12.65	12.10
9-Acridinecarboxaldehyde 2-naphthylhydrazone	$C_{24}H_{17}N_3$	347	12.29	12.10

SUMMARY

1. On the basis of electronic theory it is predicted, and shown experimentally, that a given substituent, depending on its position in the molecule, may either deepen or lighten the color.

2. Examples are given that illustrate the greater validity and power of prediction of electronic theory, as compared with pre-electronic theories of color.

3. It is emphasized that electronic theory does not displace the old pre-electronic theories of color, but lends precision to them and unifies them within itself.

4. The propert'es of five arylhydrazones of 9-acridinecarboxaldehyde are described for the first time.

LITERATURE CITED

[1] A. A. Kharkharov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 1, 117. *

[2] O. N. Witt, Ber. 21, 325 (1888); Ber. 9, 522 (1876).

[3] H. Armstrong, Proc. Chem. Soc, 27 (1882); 101, 189, 195, (1892); 101 (1902).

[4] R. Nietzki, Organ. Farbstoffe, 1888.

[5] W. Dilthey, Ber. 53, 261 (1920); 55, 1275 (1922);

[6] W. Dilthey, J. prak. Chem. 109, 2, 273 (1925).

[7] R. Wizinger, Z. angew. Chem. 40, 403, 675, 937 (1927); 39, 564 (1926).

[8] R. Wizinger, Ber. 60, 1377 (1927).

[9] R. Wizinger, Organic Dyes, United Sci. Tech. Press and Chem. Theor. Press, Leningrad, 1936, 14.

[10] A. A. Kharkharov, Trans. Leningrad Tech. Inst., 1939, p. 157.

[11] A. A. Kharkharov, Bull. Leningrad Univ., 11, 167 (1953).

[12] V. A. Izmailsky, Report of Conference on Theory of Chemical Structure, Acad. Sci. USSR Press, 1952, p. 144.

[13] A. I. Kiprianov and E. S. Timoshenko, Ukr. Chem. J., 18, 347 (1952).

[14] A. I. Kiprianov and I. N. Zhmurova, Prog. Chem., 22, No. 10, 1246 (1953).

[15] I. I. Levkoev, Report of Conference on Theory of Chemical Structure, Acad. Sci, USSR Press, 1952, p. 278.

[16] A. A. Kharkharov, J. Gen. Chem., 23, 1175 (1953).**

[17] A. E. Porai-Koshits and A. A. Kharkharov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1944, No. 1, 39.

[18] A. E. Porai-Koshits and A. A. Kharkharov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1944, No. 2-3, 143.

[19] A. E. Porai-Koshits and A. A. Kharkharov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1944, No. 4, 24.

Received April 22, 1954

S. M. Kirov Textile Institute Leningrad

---

* See Consultants Bureau Translation, p. 95

** See Consultants Bureau Translation, p. 1235

SOME PHYSICO-MECHANICAL PROPERTIES OF ESTERS OF POLYVINYL ALCOHOL

S. N. Ushakov and T. A. Kononova

Although vinyl ester polymers are now of great technological importance, there is very little information in the literature about their physico-mechanical properties. Also, most of the available data relate to fully substituted polyvinyl acetate, whereas not only the polyvinyl acetate prepared by direct polymerization of the monomer is of importance, but also partially substituted products, which may be regarded as copolymers of vinyl alcohol with vinyl acetate. The properties of such partially hydrolyzed polyvinyl acetates, and also the physico-mechanical properties of polymers of the vinyl esters of acids other than acetic, have remained almost without investigation.

The objects of our investigation included the characterization of the main physico-mechanical properties of the most important polyvinyl esters: polyvinyl formate, acetate, propionate, and butyrate of various degrees of substitution. As our main physical criteria for the appraisal of the fundamental properties of the polymers, we have selected a) the vitrification temperature T_v, and b) the tensile strength, elasticity modulus, and extension at break for two states of the polymer: vitreous, at 40° below T_v, and highly elastic, at 10° above T_v. As is well known, these criteria are of fundamental importance for the characterization of the properties of polymers. The vitrification temperature T_v is almost independent of chain length, since it is associated only with the movement of separate units of the chain. The mechanical strength of polymers is insignificant for a degree of polymerization of less than 40-80, but it then begins to increase, approximately in proportion to the increase in chain length, until the degree of polymerization reaches about 250; the curve for this relationship then bends over, and for a degree of polymerization of greater than about 600, further increase in chain length is almost without effect on the properties of the polymer. The degree of polymerization of polyvinyl esters, as generally prepared, is often less than 600, and to obtain comparable results in the determination of mechanical properties, the polymers examined must have approximately the same degree of polydispersity. We have prepared such polymers from polyvinyl alcohol by careful esterification under mild conditions [1].

For the preparation of highly substituted polyvinyl formate, we have used the method of repeated esterification with formic acid [2]. Partially formylated polyvinyl alcohols were prepared by esterification with aqueous solutions of formic acid of various concentrations. Acetic, propionic, butyric, and isobutyric esters of polyvinyl alcohol were prepared by the action of the corresponding acid anhydrides on polyvinyl alcohol in a pyridine medium. Partially esterified polyvinyl alcohols were prepared by partial hydrolysis or alkaline alcoholysis of the full esters.

In order to verify that no appreciable chain degradation had occurred during the esterification of polyvinyl alcohol and the partial saponification of polyvinyl esters under our conditions, we compared the intrinsic viscosities of the original polyvinyl alcohol and the polyvinyl alcohol regenerated by complete hydrolysis of the ester prepared from it. The intrinsic viscosities of all samples of polyvinyl alcohol regenerated in this way in our experiments were within the range 0.72-0.78, the value for the original polyvinyl alcohol being 0.74. It should be remembered that these viscosity figures refer to substances that have received a double treatment — esterification of polyvinyl alcohol, and hydrolysis of the resulting ester — whereas the esters under comparison in our investigation were prepared by one operation (esterification) from a single sample of polyvinyl alcohol.

EXPERIMENTAL

As stated above, in the study of the physico-mechanical properties of esters of polyvinyl alcohol, we have used samples of polyvinyl formate, acetate, propionate, butyrate, and isobutyrate varying in degree of substitution.

Determination of the Vitrification Temperature. The determination was carried out by two methods. As our basic method we used the dilatometric method, which gives the most accurate results, but for some samples supplementary tests were done in a Marei apparatus.

For the determination of the vitrification temperature the polymers were compressed into disks 3-4 mm thick and 1 cm in diameter, and each disk was then cut into two semicircular pieces. The compression was carried out at 40-50° above the estimated vitrification temperature, and a pressure of 50-60 kg/sq. cm was maintained for ten minutes. After a determination had been made with this sample, further determinations could be made with a more precise compression temperature. The dilatometer, containing the polymer sample immersed in mercury, was placed in a bath having a temperature 10-20° lower than the expected vitrification temperature, and was kept there for some time. The temperature was then raised at a rate of 2° in ten minutes, and readings were taken of the level of mercury in the capillary. A curve was plotted for the dependence of the mercury level V in the capillary on the temperature t, and the temperature at which a break occurred in the straight line representing the dependence of V on t was taken to be the vitrification temperature. Duplicate determinations were always in good agreement.

The results of the determinations of the vitrification temperatures of polyvinyl esters varying in degree of substitution are summarized in Table 1 and Fig. 1. In individual cases we determined T_v not only dilatometrically but also by means of the Marei apparatus. The apparatus and procedure are described in Reikh and Fainberg's book [3]. This apparatus was designed for the determination of T_v for rubbers, but we have used it successfully for the determination of the vitrification temperatures of plastics. The test sample was a compressed cylinder, diameter 0.5 cm and height 0.6-0.7 cm. The results of these tests are given in Table 2.

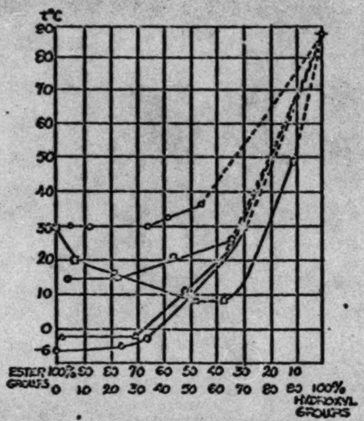


Fig. 1. ◇ - polyvinyl alcohol; ◻ - formic ester; O - acetic ester; △ - propionic ester; O - butyric ester; O - isobutyric ester.

Preparation of Films. The mechanical properties of the polyvinyl esters were determined on films. The films were cast from a 5-10% solution — on glass for polyvinyl alcohol, and on the surface of mercury for all the other polymers. The composition of the solvent was chosen according to the degree of esterification and the identity of the ester group (Table 3). In the preparation of films of polyvinyl formates some of the ester groups were hydrolyzed off by atmospheric moisture and by water contained in some of the solvent mixtures (Table 4).

In order to obtain films free from strain, it is recommended [4] that the films should be formed in an atmosphere saturated in solvent vapor. Particularly high strains arise in films cast from solutions containing a nonsolvent that evaporates more slowly than the solvent.

TABLE 1

Dependence of the Vitrification Temperatures * of Polyvinyl Esters on their Ester-group Contents

Polyvinyl formate		Polyvinyl acetate		Polyvinyl propionate		Polyvinyl butyrate		Polyvinyl isobutyrate	
Content of ester groups (mole-%)	T_v	Content of ester groups (mole-%)	T_v	Content of ester groups (mole-%)	T_v	Content of ester groups (mole-%)	T_v	Content of ester groups (mole-%)	T_v
100**	30	100***	30	98.5	−2	100.0	−6	96.7	15
99.2	30	96.5	30	72.6	−2	76.0	−4	77.0	15
93.6	20	66	30	53.4	11	67.0	−1	56.0	22
78.0	17	58.5	33	34.7	23	30.0	30	34.7	25
48.0	9	45.5	35						
36.3	9								
10.0	49								

---

* Vitrification temperatures were determined in a dilatometer.

** Polyvinyl formate prepared by the polymerization of vinyl formate.

*** Polyvinyl acetate prepared by reacetylation of polyvinyl alcohol.

In our work water acted as a nonsolvent of this sort. When a film was cast, as described above, and a part of the solvent allowed to evaporate, coagulation generally set in. For this reason, the bath of mercury covered with polymer solution was placed in a desiccator containing calcium chloride. Under these conditions the removal of water from the solution was fairly rapid, and the solution did not coagulate. Films of polyvinyl butyrate containing less than 67 mole-% of ester groups were found to be very elastic. Before these films were cast, a metal frame was placed on the mercury surface, and the film was taken from the surface in this frame and vacuum-dried, and only then was it cut from the frame. After removal from the mercury, the films were vacuum-dried to constant weight under conditions similar to the original drying of these polymers. After being dried, all of the films were kept in a vacuum desiccator over calcium chloride.

Apparatus for Testing the Films. The films were tested in a modified form of the apparatus used for determining the stability of rubber to frost [5]. The results of the tests are given in Table 5.

The following conclusions can be drawn from the foregoing results. As was to be expected, T_v is independent of the method of preparing the polyester. Values previously reported [6] for the vitrification temperatures of polyvinyl acetate and polyvinyl alcohol are 28° and 85° respectively, and we have obtained the values of 30° and 85°. No values of T_v have been reported in the literature for the other polymers that we have investigated. The unexpected coincidence of the vitrification temperatures of polyvinyl acetate and polyvinyl formate, and also the unusual course of the variation of T_v for polyvinyl formates with variation in formyl content, led us to check the values of T_v for these polymers in a Marel apparatus.

TABLE 2

Dependence of the Vitrification Temperatures* of Polyvinyl Esters on their Ester-group Contents

Polyvinyl formate		Polyvinyl acetate	
Content of ester groups (mole-%)	T_v	Content of ester groups (mole-%)	T_v
99.8	28	100	30
78.0	19	88	30
36.0	7	70	28

* Vitrification temperatures were determined in the Marel apparatus.

TABLE 3

Solvents Used in the Casting of Films

Polyvinyl acetate		Polyvinyl propionate		Polyvinyl butyrate		Polyvinyl isobutyrate	
Content of ester groups (mole-%)	Solvent	Content of ester groups (mole-%)	Solvent	Content of ester groups (mole-%)	Solvent	Content of ester groups (mole-%)	Solvent
100.0	Acetone	98.5	Ethanol	100.0	Ethanol	96.7	Ethanol
70.8	Acetone	72.6	30% Aqueous ethanol	76.4	Ethanol	77.0	Ethanol
66.0	90% Aqueous acetone	53.4	17% Aqueous ethanol	67.0	80% Aqueous ethanol	56.0	80% Aqueous ethanol
58.5	50% Aqueous acetone	34.7	25% Aqueous ethanol	35.4	50% Aqueous ethanol	34.7	60% Aqueous ethanol
45.5	66% Aqueous acetone						

TABLE 4

Degree of Hydrolysis and Content of Formic Ester Groups in Polyvinyl Formate Films after Drying

Content of ester groups before the casting of the film (mole-%)	Solvent	Content of ester groups in film (mole-%)	Proportion of hydrolyzed ester groups (mole-%)
96.6	Acetone	88.0	8.6
78.0	Acetone	69.0	9.0
68.7	(75% aqueous acetone)	60.0	8.7
48.0	(80% aqueous pyridine)	28.0	20.0
36.3	50% aqueous acetone	18.3	13.0

In the Marel apparatus, T_v is taken as the temperature at which highly elastic deformation appears. As the strain on the sample during the test is very slight (almost zero), the values of T_v determined in the dilatometer and in the Marel apparatus should coincide.

It will be seen from Table 6 that there is fairly good agreement between the values of T_v determined for these polymers by the two methods.

The vitrification temperatures of the full esters formed by polyvinyl alcohol with the normal fatty acids (excluding formic acid) fall as the size of the hydrocarbon part of the acid increases. It should be noted that the difference in the values of T_v for the acetic and propionic esters (32°) is much greater than that for the propionic and butyric esters (4°). The variations observed in T_v as we pass from polyvinyl alcohol to its esters and from one kind of ester side group to another may be explained as follows.

As is well known, the vitrification temperature depends on the extent of interaction between the polymer chains. Intermolecular forces are made up of the interactions of the atoms of the main chains and the interactions of the atoms of the side groups. In polyvinyl alcohol, Van der Waals forces act between main-chain carbons, and powerful hydrogen bonding occurs between the hydroxyl side groups. It has been calculated that the energy of molecular interaction of a polyvinyl alcohol chain 5 Å in length and having a coordination number of 4 (i.e. each chain surrounded by four other chains) amounts to 4200 kcal.

TABLE 5

Physico-mechanical Properties of Polyvinyl Esters

Ester	Content of ester groups (mole-%)	Temp of test (°C)	Tensile strength $\underline{p}$ (kg/cm^2)	Elastic modulus $\underline{E}$ (kg/cm^2)	Extension at break (%)	Temp. of test (°C)	Tensile strength $\underline{p}$ (kg/cm^2)	Elastic modulus $\underline{E}$ (kg/cm^2)	T_v, determined dilatometrically
Polyvinyl formate	100	40	63	2	2,100	−10	400	7,000	30
	88	28	76	2	1,550	−20	620	7,500	18
	69	23	72	4	1,170	−27	610	7,600	13
	60	21	28	2	1,000	−30	670	9,000	11
	23	38	162	6	1,940	−12	700	10,800	28
	18	43	164	7.2	1,460	−7	700	11,000	33
Polyvinyl acetate	100	40	47	1.0	1,900	−10	330	5,500	
	96.5	40	60	6.0	1,000	−10	400	4,000	
	58.5	43	70	3.3	1,500	−7	300	4,000	
	45.5	45	210	5.0	1,480	−5	500	6,000	
Polyvinyl propionate	98.5	8	104	10	600	−42	300	4,000	
	72.6	8	240	17	700	−42	380	4,000	
	53.4	21	263	12	1,000	−29	460	4,700	
	34.7	33	287	23	800	−17	420	8,000	
Polyvinyl butyrate	76	6	80	6	750	−44	180	2,000	
	67	9	170	17	640	−39	300	5,000	
	30	40	400	20	700	−17	700	8,400	
Polyvinyl isobutyrate	96.7	25	81	4.4	1,000	−25	300	5,000	
	77.0	25	88	4.3	910	−25	340	4,000	
	56.0	31	114	5.0	1,000	−19	350	3,000	
	34.7	35	300	10.0	800	−15	660	9,000	
Polyvinyl alcohol		95	1000	200	1,500	+45	700	5,000	

TABLE 6

Comparison of Values of the Vitrification Temperature Determined by Two Methods

Polyvinyl formate			Polyvinyl acetate		
Content of ester groups (mole-%)	Vitrification temperature		Content of ester groups (mole-%)	Vitrification temperature	
	In the Marei apparatus	In the dilatometer		In the Marei apparatus	In the dilatometer
99.8	28	30	100	30	30
78.0	19	17	88	30	30
36.0	7	9	70	28	30

TABLE 7

Interaction Energies for Hydrocarbon Groups in Fatty Acids

Group	Interaction Energy
$CH_3 \cdot CH_2-$	2,770
$CH_3 \cdot CH_2-CH_2-$	3,760
$(CH_3)_2 > CH-$	4,500

When polyvinyl alcohol is esterified with acetic acid, the hydrogen bonds disappear, and weaker Van der Waals forces appear. Also, the interactions of the main-chain carbon atoms are weakened, since the ester groups are larger than the hydroxyls and move the chains apart. Owing to the change in the character of the intermolecular forces, the molecular interactions of the polyvinyl acetate chains are reduced to 3200 kcal, and T_v is greatly lowered. When the acetyls are replaced by propionyls, the character of the intermolecular forces does not change. In themselves, the hydrocarbon groups of the propionyls show higher cohesion forces than the acetyls, so that T_V should not fall, but the increased separation of the chains greatly reduces the Van der Waals forces acting between the main-chain carbons, and this has a deciding effect on the value of the molecular interaction. The vitrification temperature of polyvinyl propionate is 32° lower than that of polyvinyl acetate.

Further separation of the chains, when considered in its relation to the character of the Van der Waals forces, should have less effect on the reduction of the interaction between chains, and therefore, the difference between polyvinyl butyrate and polyvinyl propionate in molecular interaction should be less than that between the propionate and the acetate. It is in fact found that the vitrification temperature of polyvinyl butyrate is close to that of polyvinyl propionate.

Introduction of an isoalkanoyl group increases the interaction between the chains, although such groups will screen the main chain considerably more strongly than groups of normal structure. This is confirmed by calculations, based on available data [7], of the interaction energies for the hydrocarbon groups of fatty acids (Table 7).

The cohesion forces of the isobutryl group are greater than those of the propionyl and butyryl groups, and the vitrification temperature of polyvinyl isobutyrate is therefore higher than the vitrification temperatures of the propionic and butyric esters. The fact that the vitrification temperatures of polyvinyl formate and polyvinyl acetate are identical is not altogether understandable, when only the dependence of T_V on molecular interaction forces is considered. There are indications, however, that the vitrification temperature will depend also on the heights of the potential barriers in the molecule which hinder the rotation of the chain units [8].

The higher the potential barrier in a polymer molecule, the higher the vitrification temperature. The height of the potential barrier in a polymer depends on the rigidity of the chain and, in particular on the kind of side groups present. In polyvinyl acetate the chains are farther apart than in polyvinyl formate, but movement of the units of the chain is more greatly hindered in the first polymer than in the second, since the acetate side groups are heavier than the formate groups and are bound to create a higher potential barrier. The effect of the separation of the chains by the acetate groups is neutralized by the highering of the potential barrier.

In polyvinyl acetate, the main effect on the vitrification temperature is associated with the rigidity of the chain, i.e. the quantitative change in the potential barrier as we pass from polyvinyl formate to polyvinyl acetate has a qualitative effect on the properties of the latter. It must be supposed that in esters of homologs of acetic acid, the main effect is to be associated with the separation of the chains, and quantitative changes in the potential barriers do not result in a sudden jump and qualitative change in the properties of the polymers.

It will be seen from Fig. 1 that the introduction of up to 20-30 mole-% of hydroxyl groups in the polyesters has practically no effect on the vitrification temperatures of the polyesters. When the hydroxyl content is increased further, T_V rises which may be explained by increased molecular interaction, due to the formation of strong hydrogen bonds between hydroxyls of neighboring chains.

Polyvinyl formate is exceptional. The introduction of 35 mole-% of formyl groups into polyvinyl alcohol lowers the vitrification temperature to a much greater extent than the introduction of the same proportion of the other acyl groups that we have investigated. When more than 60 mole-% of formyl groups are introduced, the vitrification temperature begins to rise. Hence, within the range 35-60 mole-% of formyl groups, there is a minimum on the curve for the dependence of the vitrification temperature on the content of ester groups. As already pointed out, the position of the minimum does not depend on the method of determining the vitrification temperature. The presence of the minimum indicates that at a formyl content of 35-55 mole-% the interaction between the chains is greatly reduced, in spite of the fact that 65-45 mole-% of free hydroxyl groups are present and that these hydroxyl groups would be expected to form hydrogen bonds between the chains, as in other esters. We consider that in the formic esters the free hydroxyls must form hydrogen bonds within the chain itself and not between the chains.

The structures of the chains of polyvinyl acetate and polyvinyl alcohol are known [9]. The diagrams in Fig. 2 show the structures of polyvinyl acetate and polyvinyl formate chains containing hydroxyl groups as well as ester groups, and they indicate that in polyvinyl formates internal hydrogen-bonding can indeed occur.

It will be seen from Fig. 2 that in both molecules the distance between the oxygen at the double bond and the hydrogen of the neighboring hydroxyl is the same (2.4 A). In polyvinyl acetate, however, the formation of a hydrogen bond is sterically hindered by a carbon-carbon bond, and this hindrance is not present in polyvinyl formate. Hence, when the formyl content is 50 mole-% and each hydroxyl hydrogen can be paired with an oxygen, internal hydrogen bonds will probably be formed. When the content of hydroxyl groups is higher than 50-60 mole-%, part of them will remain free and hydrogen bonds may be formed between the chains; the vitrification temperature then

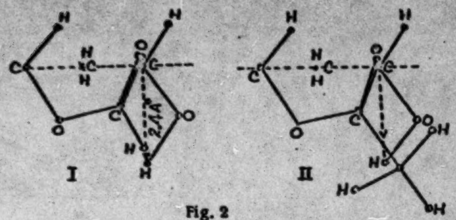


Fig. 2

rises. The vitrification temperature rises also when the formyl content rise above 60 mole-%. The replacement of hydroxyls by formic ester groups then results in increased interaction between the chains, probably as a result of the interaction of the formic ester groups themselves.

As already indicated, the mean length of the main chains was almost the same for all of the esters obtained. This made it possible for a comparison to be made of the mechanical properties of the polymers. The mechanical tests were carried out on films at various temperatures, but under conditions identical with respect to the states of the polymers: for the highly elastic state at a temperature 10° higher than T_v and for the vitreous state at a temperature 40° lower than T_v.

The results (Table 5) show that, for the highly elastic state, as the number of free hydroxyls increases, the strengths of all of the esters, apart from polyvinyl formate, also increase. It is of practical importance that the presence of up to 20-30 mole-% of hydroxyl groups, while not raising the vitrification temperature, increases the strengths of the esters. It is very important also that a considerable increase in strength is not accompanied by any appreciable change in the extension at break. For the highly elastic state, the lowest strengths (60-200 kg/sq.cm) and greatest elongations at break (2000-1500%) are given by polyvinyl acetates and formates. For the series of polyvinyl formates, the lowest strength (28 kg/sq.cm) and lowest extension (1000%) is found for polymers having a formyl content of about 60 mole-%. It may be considered that this anomaly, as also the existence of a minimum vitrification temperature for this ester, is to be associated with the formation of internal hydrogen bonds. The propionic, butyric, and isobutyric esters are approximately equal in strength (80-100 kg/sq.cm) and in extension at break (600-1000%).

The elastic modulus is low for all of the polymers in the highly elastic state (1-20 kg sq.cm). It is particularly low for polyvinyl formates (apart from these having a hydroxyl content of 80 mole-%) and polyvinyl acetates (1-5 kg/sq.cm), indicating that the interaction between chains is very weak. The polyvinyl formates, although having the lowest moduli and strengths in the highly elastic state, have the highest strengths (400-700 kg/sq.cm) and moduli (700-11.000kg/sq.cm) in the vitreous state. The other esters are very simillar to one another with respect to their strength and moduli of elasticity; the values of these properties increase as the content of free hydroxyls increases.

SUMMARY

1. For the first time the vitrification temperatures have been determined and the mechanical properties have been characterized for the full esters formed by polyvinyl alcohol with formic, propionic, butyric, and isobutyric acids, for some of the partial-hydrolysis products of these esters, and for partial acetic esters of polyvinyl alcohol..

2. It has been established that the vitrification temperatures of the investigated polyvinyl esters (except polyvinyl formate) remain constant until the content of free hydroxyls attains 30 mole-%, and then rise as the content of ester groups falls.

3. The formic esters are exceptional: the vitrification temperature passes through a minimum for a hydroxyl content of about 40-60 mole-%.

4. An explanation has been suggested for the anolmalous variation in the vitrification temperature of the formic esters of polyvinyl alcohol.

5. For all of the investigated polyvinyl esters, apart from the fully substituted butyric ester, determinations have been made of the tensile strength, elastic modulus, and extension at break of films of the polymer in the highly elastic and vitreous states.

6. It has been established that, as the proportion of free hydroxyls in the polymers increases, the tensile strengths and elasticity moduli of films prepared from them also increase. Formic esters are exceptional, since in the highly elastic state there is a minimum strength at a hydroxyl content of 40 mole-%.

7. For films in the highly elastic state, the extension at break varies very little as the proportion of free hydroxyls in the polymer rises from zero to 70 mole-%.

LITERATURE CITED

[1]. S. N. Ushakov and T. A. Kononova, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 1, 117. (1955).*

[2]. S. N. Ushakov, R. K. Gavurina, and V. P. Chekhovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 1, 71. (1947).

[3]. V. N. Reikh and V. A. Fainberg, Methods for the Technical Control of the Quality of Synthetic Rubbers and Latexes, State Chem. Press, Moscow, p. 60. (1951).

[4]. V. A. Kargin and M. I. Shtetin, J. Phys. Chem., 20, 7, 727 (1949).

[5]. G. Sh. Izraelit, Mechanical Testing of Rubber, State Chem. Press, Moscow, p. 168 (1949).

[6]. Jenekel, Kolloid. Z. 100, 163. (1942).

[7]. Yu. S. Lazurkin, J. Theor. Phys., 9, No. 14, 1261 (1939).

[8]. Ya. I. Frenkel, Kinetic Theory of Liquids, Acad. Sci. USSR Press, p. 412. (1945).

[9]. K. A. Andrianov and S. A. Yamanov, Organic Dielectrics and their Use in the Communications Industry, State Energy Press, pp. 68 and 73. (1949).

Received April 23, 1954

Lensoviet Institute of Technology
Leningrad

---

* Consultant's Bureau Translation . p. 103

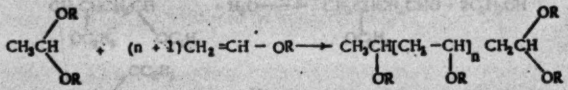
BLANK
PAGE

POLYMERIZATION OF VINYL COMPOUNDS

COMMUNICATION 2. STEPWISE SYNTHESIS OF POLY[ETHYL VINYL ETHER]

M. F. Shostakovsky and V. A. Gladyshevskaya

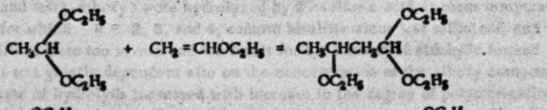
Stepwise synthesis is a new way of preparing polymers of low molecular weight. As is well known, a stepwise process proceeds gradually from one stage to another with formation of a series of products of increasing complexity, each of them being a pure individual compound. In a previous investigation [1] we have effected the stepwise synthesis of poly[butyl vinyl ether] according to the scheme:



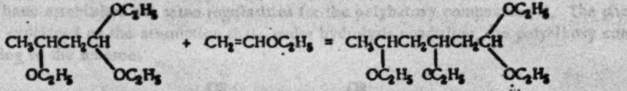
$$CH_3CH(OR)_2 + (n+1)CH_2{=}CH-OR \longrightarrow CH_3CH(OR)[CH_2-CH(OR)]_n\,CH_2CH(OR)_2$$

(n = 0, 1, 2, etc.).

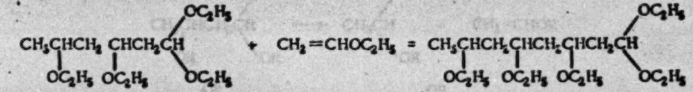
It would be expected that by the use of suitable ethers and acetals of lower boiling point in place of buytl vinyl ether and acetaldehyde dibutyl acetal the isolation of the more complex products would be facilitated, and in the present investigation we have effected the syntheses of some ethoxy compounds. The reactions proceeded according to the following schemes:



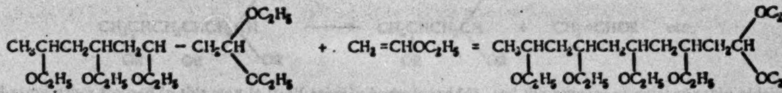
$$CH_3CH(OC_2H_5)_2 + CH_2{=}CHOC_2H_5 = CH_3CH(OC_2H_5)CH_2CH(OC_2H_5)_2 \qquad (1)$$



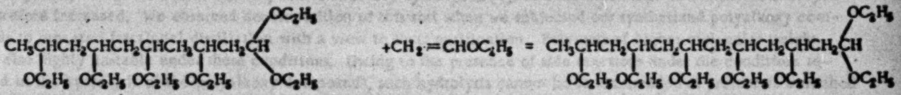
$$CH_3CH(OC_2H_5)CH_2CH(OC_2H_5)_2 + CH_2{=}CHOC_2H_5 = CH_3CH(OC_2H_5)CH_2CH(OC_2H_5)CH_2CH(OC_2H_5)_2 \qquad (2)$$



$$CH_3CH(OC_2H_5)CH_2CH(OC_2H_5)CH_2CH(OC_2H_5)_2 + CH_2{=}CHOC_2H_5 = CH_3CH(OC_2H_5)CH_2CH(OC_2H_5)CH_2CH(OC_2H_5)CH_2CH(OC_2H_5)_2 \qquad (3)$$



$$CH_3CH(OC_2H_5)CH_2CH(OC_2H_5)CH_2CH(OC_2H_5)-CH_2CH(OC_2H_5)_2 + CH_2{=}CHOC_2H_5 = CH_3CH(OC_2H_5)CH_2CH(OC_2H_5)CH_2CH(OC_2H_5)CH_2CH(OC_2H_5)CH_2CH(OC_2H_5)_2 \qquad (4)$$



$$CH_3CH(OC_2H_5)CH_2CH(OC_2H_5)CH_2CH(OC_2H_5)CH_2CH(OC_2H_5)CH_2CH(OC_2H_5)_2 + CH_2{=}CHOC_2H_5 = CH_3CH(OC_2H_5)CH_2CH(OC_2H_5)CH_2CH(OC_2H_5)CH_2CH(OC_2H_5)CH_2CH(OC_2H_5)CH_2CH(OC_2H_5)_2 \qquad (5)$$

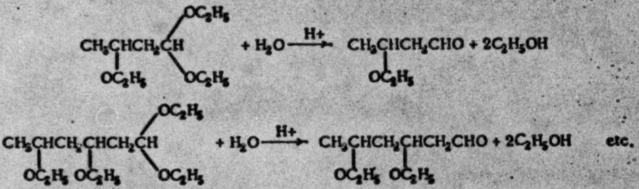
In carrying out these syntheses we were guided by the regularities that we had observed in our work on the butoxy compounds [1]. Examples of the reaction of acetals with α, β-unsaturated ethers have appeared in the literature: in a patent [2], Mueller-Cunradi and Pieroh have described the reactions of acetaldehyde acetals with vinyl ethers in presence of catalysts that promote the polymerization of vinyl ethers, and in a paper by Hoaglin and Hirsh [3] this reaction has been studied for a fairly large number of acetals and α, β-unsaturated ethers.

As a result of our experiments we have synthesized a series of ethoxy compounds – from the dimer to the hexamer inclusive. It is to be expected that stepwise synthesis will not stop short at this point, and in fact, after separation of the hexamer, the reaction mixture still contained products higher in molecular weight than the hexamer. It was not found possible, however, to isolate these products in the pure state, since they decomposed when distilled.

We have determined various constants for our products, and these are found to vary in a regular manner. Among the constants of these synthetic low-molecular-weight products, the viscosity is of special interest.

As is well known [4, 5], the viscosity of a macromolecular compound is of great importance for the determination of its molecular weight. From the relation found between molecular weight and viscosity, the constant K is calculated, and the accuracy with which this constant can be calculated is largely dependent on the care with which the macromolecular compound is fractionated. Hence, the alkoxy compounds that we have isolated, being individual low-molecular-weight products of the polmerization of vinyl ethers, can be used in the determination of the value of K characteristic of this class of polymers.

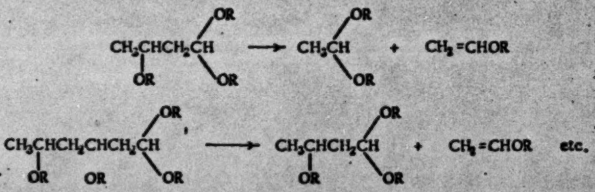
The ethoxy compounds that we have prepared were subjected to hydrolysis in order to prove the presence of terminal acetal groups:



$$CH_3CH(OC_2H_5)CH_2CH(OC_2H_5)_2 + H_2O \xrightarrow{H+} CH_3CH(OC_2H_5)CH_2CHO + 2C_2H_5OH$$

$$CH_3CH(OC_2H_5)CH_2CH(OC_2H_5)CH_2CH(OC_2H_5)_2 + H_2O \xrightarrow{H+} CH_3CH(OC_2H_5)CH_2CH(OC_2H_5)CH_2CHO + 2C_2H_5OH \quad \text{etc.}$$

The aldehyde resulting from the hydrolysis was determined quantitatively by the bisulfite method [6], and it was found that the conditions required for the hydrolysis varied for the different polyethoxy compounds. The higher the molecular weight of the ethoxy compound, the milder the conditions required for its hydrolysis. The lower members of the series (tri- and tetra-ethoxy) were hydrolyzed by 2% sulfuric acid at room temperature. For the hydrolysis of the products for which n = 2, 3, and 4, sodium bisulfite alone was sufficient, and when acid was used the hydrolysis conditions were too severe and the result for the amount of aldehyde formed was too high. The course of the hydrolysis was greatly dependent also on the concentration of the alkoxy compound and the duration of the experiment. The rate of hydrolysis increased with increase in the degree of polymerization of the ethoxy compound. We have established the same regularities for the polybutoxy compounds [1]. The phenomenon described above can be explained on the assumption that, under hydrolysis conditions, the polyalkoxy compounds are decomposed according to the scheme:



$$CH_3CH(OR)CH_2CH(OR)_2 \longrightarrow CH_3CH(OR)_2 + CH_2{=}CHOR$$

$$CH_3CH(OR)CH_2CH(OR)CH_2CH(OR)_2 \longrightarrow CH_3CH(OR)CH_2CH(OR)_2 + CH_2{=}CHOR \quad \text{etc.}$$

The alkyl vinyl ether formed in this way is itself readily hydrolyzed [6], and the amount of determinable aldehyde is therefore increased. We observed decomposition of this sort when we subjected our synthesized polyalkoxy compounds to repeated fractional distillation with a view to their purification. Polymers of higher molecular weight were also highly unstable under these conditions. Owing to the presence of side reactions under the conditions required in the hydrolysis of the polyalkoxy compounds, such hydrolysis cannot be recommended at present as a method of quantitative analysis.

EXPERIMENTAL

1. Synthesis of 1,1,3-Triethoxybutane (I). The starting materials for the synthesis were: acetaldehyde diethyl acetal, prepared by the condensation of ethyl vinyl ether with ethanol [7]; b.p. 103-104° (760 mm); d_4^{20} 0.8250; n_D^{20} 1.3824; and ethyl vinyl ether, prepared by the method of Favorsky and Shostakovsky [8]; b.p. 35-36° (760 mm); d_4^{20} 0.7535; n_D^{20} 1.3780. A 5% solution of ferric chloride in butyl alcohol was used as catalyst.

To 118 g (1 mole) of the diethyl acetal, 2 g of a 5% solution of ferric chloride in butyl alcohol was added. The mixture was heated to 45° and stirred while addition was made of 36 g (0.5 mole) of ethyl vinyl ether, the rate of addition being regulated so that the temperature remained in the range 45-50°. The experiment was continued for one hour after addition of the ether was complete. The catalyst was then precipitated by addition of 2 g of powdered anhydrous sodium carbonate. The mixture was stirred for three hours, and then filtered. The colorless liquid obtained (144 g) was vacuum-distilled, and yielded:

Fraction I.	b.p. 36-38° (15 mm):	35.6 g
Fraction II	b.p. 38-70° (10 mm):	1.2 g
Fraction III	b.p. 59-60° (3 mm):	53.2 g
Fraction IV	b.p. 61-104° (3 mm):	0.9 g
Fraction V	b.p. 104-105° (3 mm):	32.4 g
Fraction VI	b.p. 106-138° (3 mm):	0.7 g
Fraction VII	b.p. 138-139° (3 mm):	14.3 g
Residue		4.2 g

As a result of repeated fractionations, Fraction I yielded unchanged acetaldehyde diethyl acetal, b.p. 104°, d_4^{20} 0.8250; n_D^{20} 1.3824; and Fraction III yielded 1,1,3-triethoxybutane (I), b.p. 60° (3 mm); d_4^{20} 0.8743; n_D^{20} 1.4073; Found MR 53.53; for $C_{10}H_{22}O_3$ Calculated MR 53.31; Calculated M 190; found M 190; 187; viscosity 1.273 centipoise. Literature data [3]: b.p. 68° (10 mm); $d_{15.6}^{20}$ 0.878; n_D^{20} 1.4069.

Found %: C 63.02; 62.87; H 11.91; 11.70
$C_{10}H_{22}O_3$ Calculated %: C 63.11; H 11.65

Fraction V yielded 1,1,3,5-tetraethoxyhexane (II), b.p. 104° (3mm); d_4^{20} 0.9010; n_D^{20} 1.4202; Found MR 73.61; for $C_{14}H_{30}O_4$ calculated MR 73.42; found M 255; 252; calculated M 262. The literature [3] gives b.p. 107° (5 mm) $d_{15.6}^{20}$ 0.902; n_D^{20} 1.4200.

Fraction VII yielded 1,1,3,5,7-pentaethoxyoctane (III), b.p. 136-138° (3 mm); d_4^{20} 0.9160; n_4^{20} 1.4280; found MR 93.80; for $C_{18}H_{38}O_5$ calculated MR 93.54; found M 325; 328; calculated M 334. The literature [3] gives b.p. 110-116° (0.5 mm); $d_{15.6}^{20}$ 0.917; n_D^{20} 1.4281.

The intermediate fractions (II, IV, and VI) were not investigated because of their very small amounts.

2. Synthesis of 1,1,3,5-Tetraethoxyhexane (II). The reactants were 95 g (0.5 mole) of 1,1,3-triethoxybutane, b.p. 60-61° (3 mm), d_4^{20} 0.8739; n_D^{20} 1.4070 , and 18 g (0.25 mole) of ethyl vinyl ether. The reaction conditions were the same as those of Experiment 1. The product was 108 g of a slightly colored liquid, which was vacuum-distilled.

As a result of numerous fractionations the following compounds were isolated: a) unchanged 1,1,3-triethoxybutane (43.7 g), b.p. 60-62° (3 mm), d_4^{20} 0.8740; n_D^{20} 1.4068; b) 1,1,3,5-tetraethoxyhexane (II) (28.4 g), b.p. 103-104°; d_4^{20} 0.9004; n_D^{20} 1.4200; found MR 73.63; for $C_{14}H_{30}O_4$. calculated MR 73.42; found M 256, 254; calculated M 262; viscosity 3.253 centipoise (see Experiment 1, Fraction V);

Found %: C 64.03; 64.21; H 11.68; 11.21
$C_{14}H_{30}O_4$. Calculated %: C 64.08; H 11.50

c) 1,1,3,5,7-pentaethoxyoctane (III) (10.3 g), b.p. 137-139° (3 mm); d_4^{20} 0.9170; n_D^{20} 1.4280; found MR 93.70; for $C_{18}H_{38}O_5$ calculated MR 93.54; found M 324; 320; calculated M 334 (see Experiment 1, Fraction VII); d) 1,1,3,5,7,9-hexaethoxydecane (IV) (8.4 g), b.p. 168-170° (3 mm); d_4^{20} 0.9338; n_D^{20} 1.4360; found MR 113.68 for $C_{22}H_{46}O_6$; calculated MR 113.65; found M 399; 395; calculated M 406; viscosity 17.846 centipoise.

Found %: C 64.60; 64.40; H 11.25; 11.46
$C_{22}H_{46}O_6$. Calculated %: C 64.98; H 11.40

In this synthesis we prepared the compound for the first time.

3. Synthesis of 1,1,3,5,7-Pentaethoxyoctane (III). The reactants were 132 g (0.5 mole) of 1,1,3,5-tetraethoxyhexane, b.p. 103-104° (3 mm), d_4^{20} 0.9004; n_D^{20} 1.4200, and 24 g (0.33 mole) of ethyl vinyl ether. The reaction conditions were the same as those of Experiment 1. The product was 142 g of a slightly colored liquid, which was distilled repeatedly under reduced pressure. Apart from unchanged 1,1,3,5-tetraethoxyhexane (65.4 g), the following products were obtained: a) 1,1,3,5,7-pentaethoxyoctane (III) (27.3 g), b.p. 137-139° (3 mm); d_4^{20} 0.9166; n_D^{20} 1.4283; found MR 93.81; for $C_{18}H_{38}O_5$ calculated MR 93.54; found M 330; 326; calculated M 334; viscosity 7.650 centipoise [see Experiment 1, Fraction VII and Experiment 2, compound (c)].

Found %: C 64.48; 64.24; H 11.27; 11.36
$C_{18}H_{38}O_5$. Calculated %: C 64.63 H 11.45

b) 1,1,3,5,7,9-hexaethoxydecane (IV) (15.6 g) b.p. 168-170° (3 mm) ; d_4^{20} 0.9340; n_D^{20} 1.4365; found MR 113.77; for $C_{22}H_{46}O_6$ calculated MR 113.65; found M 392; 389; calculated M 406 [see Experiment 2, compound (d)];

c) 1,1,3,5,7,9,11-heptaethoxydodecane (V) (12.3 g) b.p. 190-193° (3 mm); d_4^{20} 0.9407; n_D^{20} 1.4390; found MR 133.65; for $C_{26}H_{54}O_7$ calculated MR 133.77; found M 489, 483; calculated M 478.

Found %: C 65.48; 65.26; H 11.30; 11.09

$C_{26}H_{54}O_7$. Calculated %: C 65.23; H 11.37

In this synthesis we prepared the compound for the first time.

4 Hydrolysis of the Ethoxy Compounds. a) The hydrolysis of 1,1,3-triethoxybutane and 1,1,3,5-tetraethoxyhexane was carried out in a flask containing 10 ml of 2% sulfuric acid and 20 ml of 0.2 N sodium bisulfite, the weighed amount of substance (0.025-0.150 g) being added in a small sealed tube, which was broken by shaking the flask vigorously. Excess of bisulfite was titrated with 0.1 N iodine – after 60 minutes for 1,1,3-triethoxybutane, and after 30 minutes for 1,1,3,5-tetraethoxyhexane. b) The hydrolysis of the penta-, hexa-, and hepta-ethoxy compounds was carried out in absence of sulfuric acid, 20 ml of 0.2 N sodium bisulfite being added as before. The conditions were the same in other respects. Excess of bisulfite was titrated after two hours for 1,1,3,5,7-pentaethoxyoctane, and after 30 minutes for 1,1,3,5,7,9-hexaethoxydecane; for 1,1,3,5,7,9,11-heptaethoxydodecane, the titration was performed immediately after addition of the substance to the bisulfite solution.

In each case a parallel control experiment was carried out. The degree of hydrolysis was calculated by the formula derived previously [6]. The results of the hydrolysis of the ethoxy compounds are given in the table.

TABLE

Hydrolysis of Ethoxy Compounds

Ethoxy compound	Extent of hydrolysis of ethoxy compound (%)
1,1,3-Triethoxybutane	95.9 96.3
1,1,3,5-Tetraethoxyhexane	96.5 96.7
1,1,3,5,7-Pentaethoxyoctane	96.8 98.1
1,1,3,5,7,9-Hexaethoxydecane	96.9 97.0
1,1,3,5,7,9,11-Hepraethoxydodecane	97.1 97.8

SUMMARY

1. The stepwise synthesis of pure individual members of the poly[ethyl vinyl ether] series has been effected.

2. The following substances have been isolated and characterized: 1,1,3-triethoxybutane, 1,1,3,5-tetraethoxyhexane, 1,1,3,5,7-pentaethoxyoctahe; 1,1,3,5,7,9-hexaethoxydecane, and 1,1,3,5,7,8,11-heptaethoxydodecane.

Received December 30, 1953

N. D. Zelinsky Institute of Organic Chemistry of the USSR
Academy of Sciences

LITERATURE CITED

[1] M. F. Shostakovsky and V. A. Gladyshevskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, No. 1, 146.

[2] M. Mueller-Gunradi, K. Pieroh, U. S. Patent 2,165,962 (1939).

[3] R. Hoaglin, D. Hirsh, J. Am. Chem. Soc. 10, 3468 (1949).

[4] H. Staudinger, Macromolecular Organic Compounds, United Sci. Tech. Press and Chem. Theor. Press, Leningrad, 1935, p. 53.

[5] L. P. Losev and G. S. Petrov, Chemistry of Synthetic Resins, State Chem. Press, 1951.

[6] M. F. Shostakovsky and E. N. Prilezhaeva, J. Gen. Chem. 17, 6 (1947).

[7] M. F. Shostakovsky and N. A. Gershtein, J. Gen. Chem., 16, 937 (1946).

[8] A. E. Favorsky and M. F. Shostakovsky, J. Gen. Chem., 13, 1 (1943).

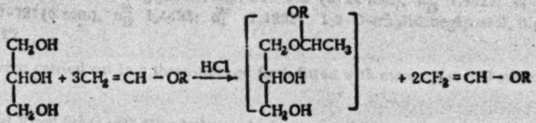
REACTIONS BETWEEN VINYL COMPOUNDS AND MULTIFUNCTIONAL COMPOUNDS

COMMUNICATION 4. REACTION OF ALKYL VINYL ETHERS WITH GLYCEROL AND WITH GLYCEROL 1,2- AND 1,3-CYCLIC ACETALS

M. F. Shostakovsky, V. V. Zhebrovsky, and M. A. Medelyanovskaya

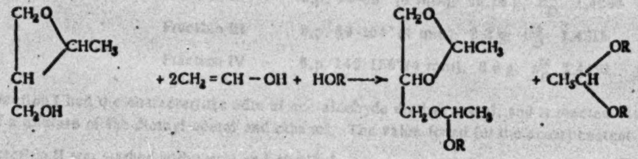
The present paper describes a study of the reaction of alkyl vinyl ethers with glycerol and with glycerol 1,2- and 1,2-cyclic acetals (1,2- and 1,3-O-ethylideneglycerols) in presence of traces of hydrochloric acid; the work forms an extension of our investigations on the synthesis of cyclic acetals of glycerol and of derivatives of these. We have already shown [1] that reaction of equimolecular proportions of ethyl vinyl ether and glycerol yields a mixture consisting mainly of 1,2- and 1,3-O-ethylideneglycerols, and that the same reaction with butyl vinyl ether yields 1,2-O-ethylideneglycerol as the main product. In the present investigation we have established that reaction of alkyl vinyl ethers with glycerol in the molar ratio of 3:1 yields, in addition to other acetals, mixed acetals of glycerol and monohydric alcohols. Thus, the concentrations of the reactants have a considerable effect on the course of the acetal-formation reaction, and by varying them we may direct the synthesis in the desired direction.

When ethyl vinyl ether or butyl vinyl ether reacts with glycerol in the proportions indicated above, it is clear that, in the first place, the corresponding mixed acetal of glycerol and the monohydric alcohol (I) must be formed:



(I)

The mixed acetal of glycerol (I) will then undergo a change leading to the formation of 1,2-O-ethylideneglycerol (II), with elimination of the free alcohol. The cyclic acetal (II) will react with the alkyl vinyl ether and form the complex acetal of glycerol (III), and at the same time the free monohydric alcohol will react with the alkyl vinyl ether with formation of the corresponding acetal (IV):

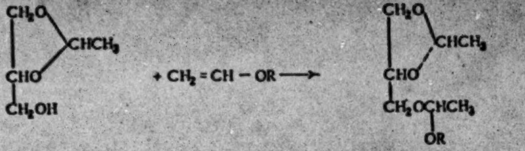


(II) (III) (IV)

(R is C_2H_5 or C_4H_9).

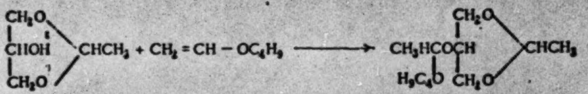
Under these conditions, however, the formation of an acetal of glycerol in which all three hydroxyls would be replaced by alkoxyethoxy groups is excluded, since the cyclization reaction occurring after the formation of the acetal (I) is more rapid than the addition of the alkyl vinyl ether to the other hydroxyls of glycerol.

In order to verify our suggested mechanism of the reaction leading to the formation of the acetals (III) when glycerol is treated with alkyl vinyl ethers, we attempted to synthesize these acetals from alkyl vinyl ethers and the 1,2- and 1,3-O-ethylideneglycerols described previously [2]. An investigation of the products formed by the addition of ethyl vinyl and butyl vinyl ethers to 1,2-O-ethylideneglycerol gave us every reason to suppose that the formation of the acetal (III) did indeed occur according to the scheme:



($R = C_2H_5$ or C_4H_9).

In this reaction we isolated 3-O-(1-ethoxyethyl)-1,2-O-ethylideneglycerol and 3-O-(1-butoxyethyl)-1,2-O-ethylideneglycerol. We found also acetals of the corresponding monohydric alcohols, formed as by-products, evidently as a result of the disproportionation of the acetal (III). When butyl vinyl ether reacted with 1,3-O-ethylideneglycerol, the acetal (V) was formed:



(V)

In order to prove the structures of the acetals obtained, they were hydrolyzed, and the hydrolysis products were characterized.

EXPERIMENTAL

The starting materials were: ethyl vinyl ether, b.p. 35-36°, n_D^{20} 1.3782; d_4^{20} 0.7533; butyl vinyl ether, b.p. 93-94°, n_D^{20} 1.4030; d_4^{20} 0.7795; glycerol, b.p. 164-172° (8-14 mm), n_D^{20} 1.4728; d_4^{20} 1.2582; 1,2-O-ethylideneglycerol, b.p. 70-72° (5 mm), n_D^{20} 1.4435; d_4^{20} 1.1232; 1,3-O-ethylideneglycerol, b.p. 60-60.5° (8 mm), n_D^{20} 1.4519; d_4^{20} 1.1422.

The syntheses were carried out in a three-necked flask fitted with mercury-sealed stirrer, thermometer, and reflux condenser.

Reaction of Ethyl Vinyl Ether with Glycerol at a Molar Ratio of 3:1. The reaction mixture consisted of 18.4 g (0.2 mole) of glycerol, 43.2 (0.6 mole) of ethyl vinylether, and 6 drops (0.08 g) of hydrochloric acid. A rise in temperature up to 101° was observed after 60 minutes. After being neutralized with potassium carbonate, the reaction product was fractionally distilled, and yielded:

Fraction I	B.p. 84-95°; 27.7 g; n_D^{20} 1.3835
Fraction II	B.p. 74-86° (4 mm); 20.18 g; n_D^{20} 1.4280
Fraction III	B.p. 89-104° (4 mm); 2.3 g; n_D^{20} 1.4315
Fraction IV	B.p. 149-156° (4 mm); 6.6 g; n_D^{20} 1.4492

Fraction I had the characteristic odor of acetaldehyde diethyl acetal, and it reacted with sodium, i.e. consisted of a mixture of the diethyl acetal and ethanol. The value found for the acetal content was 93.25; 93.29%.

Fraction II was washed with water and distilled. Its constants [b.p. 86-87° (7 mm); d_4^{20} 1.0088; n_D^{20} 1.4255; found MR 48.26; calculated for $C_5H_{18}O_4$ MR 48.134] corresponded to 3-O-(1-ethoxyethyl)-1,2-O-ethylideneglycerol. Acetal content 98.61; 98.41%. Yield of acetal 9.2 g (23.9%).

	Found %:	C 56.20; 56.26;	H 9.54; 9.63
$C_9H_{18}O_4$:	Calculated %:	C 56.82;	H 9.53

Reaction of Butyl Vinyl Ether with Glycerol at a Molar Ratio of 3:1. A mixture of 11.5 g (0.125 mole) of glycerol, 37.5 g (0.375 mole) of butyl vinyl ether, and 3 drops (0.042 g) of hydrochloric acid (catalyst) was heated at 50° for four hours. After being neutralized with potassium carbonate, the reaction product was fractionally distilled, when it yielded:

Fraction I, B.p. 66-90°; 18.0 g
Fraction II, B.p. 104-118°; 12.2 g
Fraction III, Undistilled residue, 18.36 g; n_D^{20} 1.4350

Fraction I was a mixture of acetaldehyde dibutyl acetal and butyl alcohol. Redistillation yielded a product of b.p. 64-68° (5-7 mm) and n_D^{20} 1.4112; and the dibutyl acetal content found for this was 91.69; 92.63%.

Fraction II yielded a substance (7.4 g) having b.p. 105-106° (5 mm); n_D^{20} 1.4312; d_4^{20} 0.9816; found MR 57.59; calculated for $C_{11}H_{22}O_4$ MR 57.37. It was 3-O-(1-butoxyethyl)-1,2-O-ethylidendglycerol, obtained in 27.2% yield.

	Found %:	C 60.46; 60.33;	H 10.35; 10.21
$C_{11}H_{22}O_4$.	Calculated %:	C 60.52;	H 10.11

Synthesis of 3-O-(1-Ethoxyethyl)-1,2-O-ethylideneglycerol from Ethyl Vinyl Ether and 1,2-O-Ethylideneglycerol. A mixture of 7 g of 1,2-O-ethylideneglycerol and 4.27 g of ethyl vinyl ether was prepared in a flask, and one drop (0.014 g) of hydrochloric acid was added, when the temperature of the reaction mixture rose to 90°. The reaction product was neutralized with potassium carbonate and then fractionally distilled from a Favorsky flask. The amount taken for fractionation was 10.95 g, and the fractions isolated were:

Fraction I, b.p. 68-75° (5 mm); 3.07 g; n_D^{20} 1.4312
Fraction II, b.p. 75-78° (5 mm); 4.34 g. n_D^{20} 1.4278
Fraction III, b.p. 78-79° (5 mm); 1.45 g; n_D^{20} 1.4282
Residue 0.3 g

Fractions II and III, after treatment with sodium, yielded 2.3 g of 3-O-(1-ethoxyethyl)-1,2-O-ethylideneglycerol, b.p. 84-86° (7 mm); n_D^{20} 1.4275; d_4^{20} 1.0090; found MR 48.45; calculated for $C_9H_{18}O_4$ MR 48.13; the yield of acetal was 20.4%.

	Found %:	C 56.64; 56.61;	H 9.47; 9.48
$C_9H_{18}O_4$.	Calculated %:	C 56.82;	H 9.53

Synthesis of 3-O-(1-Butoxyethyl)-1,2-O-ethylideneglycerol from Butyl Vinyl Ether and 1,2-O-Ethylideneglycerol. The reactants were 8.85 g of 1,2-O-ethylideneglycerol, 7.5 g of butyl vinyl ether, and one drop (0.014 g) of hydrochloric acid. When the catalyst was added, there was a rise in temperature to 87°. Fractional distillation of 15.85 g yielded:

Fraction I, b.p. 64-104° (8 mm); 1.02 g; n_D^{20} 1.4262
Fraction II, b.p. 112-114°; 13.4 g; n_D^{20} 1.4318
Residue 1.10 g; n_D^{20} 1.4450

Refractionation of Fraction II yielded 10.90 g of 3-O-(1-butoxyethyl)-1,2-O-ethylideneglycerol, b.p. 115-117° (8-9 mm); d_4^{20} 0.9816; n_D^{20} 1.4312; found MR 57.57; calculated for $C_{11}H_{22}O_4$ MR 57.37. Acetal content 98.20; 98.31%. Yield 66.6%.

	Found %:	C 60.65; 60.68;	H 10.15; 10.19
$C_{11}H_{22}O_4$.	Calculated %:	C 60.52;	H 10.11

Hydrolysis of 3-O-(1-Butoxyethyl)-1,2-O-ethylideneglycerol. The acetal (5 g) was heated with 20 ml of 2% sulfuric acid in a water bath for one hour. The resulting solution was cooled, saturated with potassium carbonate, and extracted with ether. The residue after removal of ether was 1.1 g (61%) of butyl alcohol, b.p. 115-116° and n_D^{20} 1.4002.

Synthesis of 2-O-(1-Butoxyethyl)-1,3-O-ethylideneglycerol from Butyl Vinyl Ether and 1,3-O-Ethylideneglycerol. Reaction of 4.1 g of 1,3-O-ethylideneglycerol with 3.47 g of butyl vinyl ether in presence of one drop of hydrochloric acid was accompanied by a rise in temperature to 70°. Distillation yielded:

Fraction I, b.p. 63-106° (5 mm); 1.54 g; n_D^{20} 1.4222

Fraction II, b.p. 112-116° (5 mm); 3.9 g; n_D^{20} 1.4401

Residue 1.5 g; n_D^{20} 1.4620

Refractionation of Fraction II yielded 2.70 g of a substance having b.p. 106-107° (3-4 mm); d_4^{20} 1.0025; n_D^{20} 1.4410; found M 217.3; 218.8; calculated for $C_{11}H_{22}O_4$ M 218.28; found MR 57.43; calculated MR 57.37. Acetal content 98.78; 98.31%. The yield of 2-O-(1-butoxyethyl)-1,3-O-ethylideneglycerol was 35.6%.

	Found %:	C 60.30; 60.17;	H 10.21; 10.13
$C_{11}H_{22}O_4$.	Calculated %:	C 60.52;	H 10.11

SUMMARY

1. The following reactions have been investigated: the interaction of ethyl vinyl ether and of butyl vinyl ether

with glycerol at a molar ratio of 3 : 1; the addition of ethyl vinyl ether and of butyl vinyl ether to 1,2-O-ethylideneglycerol; and the addition of butyl vinyl ether to 1,3-O-ethylideneglycerol.

2. It has been shown, for the first time, that the main products of the reactions of ethyl vinyl and butyl vinyl ethers with glycerol are 3-O-(1-ethoxyethyl)-and 3-O-(1-butoxyethyl)-1,2-O-ethylideneglycerols (III) and acetals of the corresponding monohydric alcohols (IV).

3. By the reaction of 1,2-O-ethylideneglycerol with ethyl vinyl and with butyl vinyl ethers, complex cyclic acetals of glycerol (III) are formed.

4. 2-O-(1-Butoxyethyl)-1,3-O-ethylideneglycerol (V) has been synthesized for the first time from 1,3-O-ethylidene glycerol and butyl vinyl ether.

LITERATURE CITED

[1] M. F. Shostakovsky, V. V. Zhebrovsky, and M. A. Medelyanovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 1, 166. *

[2] M. F. Shostakovsky, V. V. Zhebrovsky, and M. A. Medelyanovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 4, 683. **

Received January 13, 1954

N. D. Zelinsky Institute of Organic Chemistry of the
USSR Academy of Sciences

---

* See Consultants Bureau Translation, p. 137.

** See Consultants Bureau Translation, p. 583.

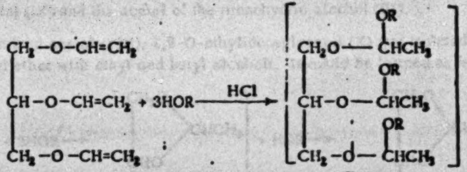
REACTIONS BETWEEN VINYL COMPOUNDS AND MULTIFUNCTIONAL COMPOUNDS

COMMUNICATION 5. REACTION OF GLYCEROL TRIVINYL ETHER WITH MONOHYDRIC ALCOHOLS

M. F. Shostakovsky, V. V. Zhebrovsky, and M. A. Medelyanovskaya

In connection with our study of the chemistry of the formation of acetals from vinyl ethers and polyhydric alcohols, it was considered to be of interest to investigate the reactions of a multifunctional vinyl ether with monohydric alcohols, particularly as we had already studied the reaction of acetal formation from polyhydric alcohols and monovinyl ethers [1,2]. We have already shown [3] that in the reaction of multifunctional vinyl ether (glycerol trivinyl ether) with glycols (ethylene glycol and 1,4-butanediol) the main products are cyclic acetals of the glycols and glycerol.

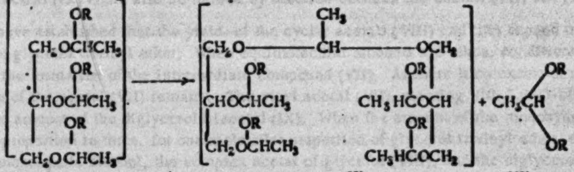
In the present investigation glycerol trivinyl ether has been selected as the multifunctional vinyl ether, and ethyl and butyl alcohols as monohydric alcohols. It appeared possible that interaction between these compounds in presence of traces of hydrochloric acid would lead in the first place to the formation of acetals of glycerol and monohydric alcohols of structure:



(I)

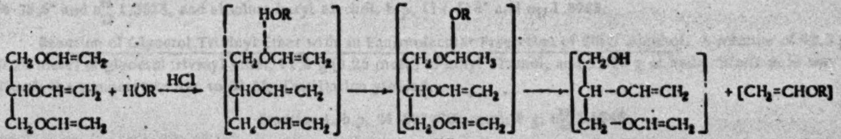
($R = C_2H_5$ or C_4H_9) and the corresponding mono- and di-acetals.

Disproportionation of acetals such as (I) could result in the formation of the following compounds:



(II) (III)

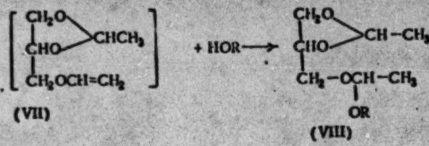
Further disproportionation of the acetal (II) could lead to the formation of still more complicated compounds of a similar type. However, an examination of the products formed by the reaction of glycerol trivinyl ether with monohydric alcohols gave reason to suppose that the formation of acetals of glycerol occurred in the following way:



(IV) (V) (VI)

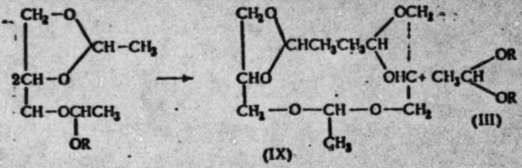
($R = C_2H_5$ or C_4H_9).

The first product is the mixed acetal (IV) of glycerol divinyl ether and the monohydric alcohol, and this, being unstable, readily undergoes change with formation of the partial vinyl ether of glycerol (V) and the vinyl ether of the monohydric alcohol. The compound (V) then isomerizes to the vinyl acetal (VII), which, reacting further with the monohydric alcohol, yields 3-O-(1-alkoxyethyl)-1,2-O-ethylideneglycerol (VIII):



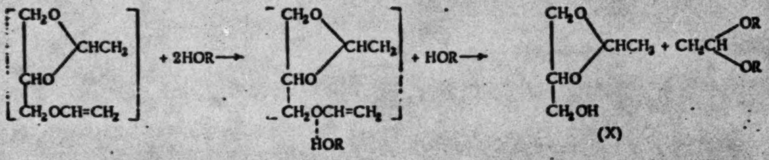
By reaction with the alcohol, the vinyl ether of this alcohol (VI), formed by the transetherification reaction, may form the corresponding acetal (III).

By disproportionation, the complex acetal (VIII) may give:



i.e. the diglycerol triacetal (IX) and the acetal of the monohydric alcohol (III).

In addition to the mixed acetal (VIII), 1,2-O-ethylideneglycerol (X) was isolated from the products of the reaction of glycerol trivinyl ether with ethyl and butyl alcohols. It could be formed as follows:



The acetal (IX) could also be formed by reaction between the acetals (VII) and (X).

We have established that the yields of the cyclic acetals (VIII) and (IX) depend on the proportions of monohydric alcohol and glycerol trivinyl ether. When equimolecular amounts are taken, conditions are favorable for reaction leading to the formation of the intermediate compound (VII). As there is no excess of monohydric alcohol, the free vinyl group of the acetal (VII) remains. The vinyl acetal (VII), reacting with 1,2-O-ethylideneglycerol (X), yields an appreciable amount of the diglycerol triacetal (IX). When the amount of the monohydric alcohol is raised from one molecular proportion to three, for one molecular proportion of glycerol trivinyl ether, experiment shows that the acetal of the monohydric alcohol, the complex acetal of glycerol (VIII), and the diglycerol triacetal (IX) are formed, and the yield of the triacetal (IX) is reduced.

EXPERIMENTAL

The starting substances were glycerol trivinyl ether, b.p. 164-165° and n_D^{20} 1.4385, absolute ethyl alcohol, b.p. 78-78.5° and n_D^{20} 1.3618, and absolute butyl alcohol, b.p. 117-118° and n_D 1.3998.

Reaction of Glycerol Trivinyl Ether with an Equimolecular Proportion of Ethyl Alcohol. A mixture of 42.5 g (0.25 mole) of glycerol trivinyl ether, 11.5 g (0.25 mole) of ethyl alcohol, and 0.028 g of hydrochloric acid was stirred; the temperature rose to 98.5°. Distillation yielded:

Fraction I, b.p. 74-88° (760 mm); 8 g; n_D^{20} 1.3845
Fraction II b.p. 83-95° (7-8 mm); 23.88 g; n_D^{20} 1.4270
Fraction III b.p. 154-157° (7-8 mm); 18.82 g n_D^{20} 1.4478
Residue 1.6 g

Refractionation of Fraction I yielded 7 g of acetaldehyde diethyl acetal, b.p. 98-100°, n_D^{18} 1.3840 (the literature [4] gives b.p. 103.7-104° and n_D^{20} 1.3820). Analysis by hydrolysis followed by oxime formation gave an acetal content of 104.3; 104.7%. The somewhat high analytical results and the slight departures of the constants from reported values are to be explained by the presence of 3-O-(1-ethoxyethyl)-1,2-O-ethylideneglycerol, the removal of which did not appear to be possible.

Fraction II (15 g) was redistilled twice, and a substance (11.7 g) was isolated which had b.p. 83-84° (6 mm); n_D^{20} 1.4260; d_4^{20} 1.0098; found M 191.0; 189.73; calculated for $C_9H_{18}O_4$ M 190.23; found MR 48.30; calculated MR 48.13 [5]. This substance was 3-O-(1-ethoxyethyl)-1,2-O-ethylideneglycerol (VIII). The acetal content was 98.49; 99.12%.

Fraction II (7 g) was benzoylated, and the benzoic ester of 1,2-O-ethylideneglycerol (1.64 g) was obtained. It had b.p. 147-148° (5 mm) and n_D^{20} 1.5141 [6].

Found %: C 64.73; 64.52; H 6.32; 6.41

$C_{12}H_{14}O_4$. Calculated %: C 64.86 H 6.31

Fraction III was redistilled and yielded 16.4 g of a substance that was found to be the acetal derived from three molecules of acetaldehyde and two of glycerol. Its constants were b.p. 153-154° (6 mm), d_4^{20} 1.1072; and n_D^{20} 1.4481, and the literature [7] gives b.p. 160-162° (14 mm), d_4^{24} 1.1067, and n_D^{20} 1.4482. Found M 262.8; 261.7 (cryoscopically in benzene); calcaulated for $C_{12}H_{22}O_6$: M 262.29. Found MR 63.66; Calculated MR 63.074.

Reaction of Glycerol Trivinyl Ether with Ethyl alcohol in the Molar Ratio 1 : 3. A mixture of 42.5 g (0.25 mole) of glycerol trivinyl ether and 34.5 g (0.75 mole) of ethyl alcohol was prepared in a flask, and two drops (0.028 g) of hydrochloric acid were added. The temperature rose to 87°. Fractionation of the reaction product yielded:

Fraction I, b.p. 74-84°; 34.06 g; n_D^{20} 1.3770

Fraction II, b.p. 71-90° (6 mm); 27.1 g; n_D^{20} 1.4350

Fraction III, b.p. 150-155° (6 mm); 13.4 g; n_D^{20} 1.4492

Residue 1.05 g

When redistilled, Fraction I boiled in the same range. It was a mixture of ethyl alcohol and acetaldehyde diethyl acetal. By hydrolysis and oxime formation it was shown that it contained 43.52% (duplicate 43.46%) of the diethyl acetal.

An ethereal solution of Fraction II was washed twice with water. The ether layer was dried with potassium carbonate and distilled, when 10.4 g of 3-O-(1-ethoxyethyl)-1,2-O-ethylideneglycerol (VIII) was obtained. Its constants were: b.p. 86-87° (7 mm); d_4^{20} 1.0090; n_D^{20} 1.4262; found: MR 48.28; calculated for $C_9H_{18}O_4$ MR 48.134. Acetal content 97.71; 98.28%.

Saturation of the wash water with potassium carbonate and extraction with ether yielded 3.6 g of 1,2-O-ethylideneglycerol, having the constants: b.p. 75-77° (8 mm); d_4^{20} 1.1236; n_D^{20} 1.4436; found MR 27.90; calculated for $C_5H_{10}O_3$ MR 27.90. The literature [6] gives b.p. 68-70° (1 mm), d_4^{17} 1.1243; n_D^{17} 1.4415.

After being redistilled, Fraction III boiled at 157-160° (7 mm) and had d_4^{20} 1.1070; n_D^{20} 1.4483. It was the diglycerol triacetal [7].

Reaction of Glycerol Trivinyl Ether with an Equimolecular Proportion of Butyl Alcohol. In the reaction of 34 g (0.2 mole) of glycerol trivinyl ether and 14.82 g (0.2 mole) of butyl alcohol in presence of two drops of hydrochloric acid (0.028 g), a rise in temperature to 83° was observed. Fractional distillation yielded:

Fraction I, b.p. 56-91° (6 mm); 13.26 g; n_D^{20} 1.4250

Fraction II, b.p. 108-110° (6 mm); 25.20 g; n_D^{20} 1.4322

Fraction III, b.p. 149-152° (6 mm); 7.0 g; n_D^{20} 1.4470

Residue 1.6 g

Fraction I, which boiled over a wide range of temperature, was diluted with ether and washed with water. It was not found possible to isolate completely pure acetaldehyde dibutyl acetal from the ether layer, even after repeated distillation. The product isolated (6 g) boiled at 164-165° and had n_D^{20} 1.4150 (the literature [8] gives b.p. 185-186° and n_D^{20} 1.4085). The diacetal content was found to be 87.13; 87.55%. The aqueous layer yielded 0.25 g of 1,2-O-ethylideneglycerol, b.p. 88° (15 mm); n_D^{20} 1.4420 [6].

Redistillation of Fraction II yielded 19.2 g of 3-O-(1-butoxyethyl)-1,2-O-ethylideneglycerol (VIII), the constants of which were b.p. 108-108.5° (6 mm); d_4^{20} 0.9310; n_D^{20} 1.4310; found M 211.9; 219.8; calculated for $C_{11}H_{22}O_4$

M 218.28; found MR 57.17; calculated for $C_{11}H_{22}O_4$ MR 56.95 [5]. The acetal content (by hydrolysis and oxime formation) was 99.79; 99.46%.

Redistillation of Fraction III yielded 5 g of a substance boiling at 151-153° (6 mm) and having n_D^{20} 1.4478. Its constants corresponded to the diglycerol triacetal (IX).

SUMMARY

1. The reactions of glycerol trivinyl ether with ethyl and butyl alcohols have been studied.

2. It has been shown that the main reaction products in the reaction of glycerol trivinyl ether with monohydric (ethyl and butyl) alcohols are the acetaldehyde acetals of the monohydric alcohols, mixed acetals of glycerol and the monohydric alcohol (VIII), and the acetal derived from three molecules of acetaldehyde and two of glycerol (IX).

3. 3-O-(1-Ethoxyethyl)- and 3-O-(1-butoxyethyl)-1,2-O-ethylideneglycerols (VIII) have been isolated and characterized.

4. It has been shown that the reaction of glycerol trivinyl ether with ethyl and butyl alcohols yields the same acetals as those formed by the reaction of ethyl vinyl and butyl vinyl ethers with glycerol.

LITERATURE CITED

[1] M. F. Shostakovsky, V. V. Zhebrovsky, and M. A. Medelyanovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 1, 166.*

[2] M. F. Shostakovsky, V. V. Zhebrovsky, and M. A. Medelyanovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 3, 535.**

[3] M. F. Shostakovsky, V. V. Zhebrovsky, and M. A. Medelyanovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 4, 683.***

[4] M. F. Shostakovsky, Vinyl Ethers, Acad. Sci. USSR Press, 1952, 203.

[5] M. F. Shostakovsky, V. V. Zhebrovsky, and M. A. Medelyanovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, No. 2, 350.****

[6] A. C. Hill, H. Hibbert, J. Am. Chem. Soc. 50, 8, 2242-2249 (1928).

[7] I. A. Nieuwland, R. R. Vogt, W. H. Foohey, J. Am. Chem. Soc. 1018 (1930).

[8] N. A. Gershtein and M. F. Shostakovsky, J. Gen. Chem., 16, No. 6, 937 (1946).

Received January 13, 1954

N. D. Zelinsky Institute of Organic Chemistry of the
USSR Academy of Sciences

---

* See Consultants Bureau Translation, p. 137.

** See Consultants Bureau Translation, p. 455.

*** See Consultants Bureau Translation, p. 583.

**** See Consultants Bureau Translation, p. 313.

MACROMOLECULAR COMPOUNDS . LXXI.

COMMUNICATION 71. POLYCONDENSATION OF 1,2-CHLOROETHANE WITH CHLOROBENZENE IN PRESENCE OF ALUMINUM CHLORIDE

G. S. Kolesnikov, V. V. Korshak, and L. S. Fedorova

Continuing our study [1-3] of polycondensation processes occurring between aliphatic halogen compounds and aromatic hydrocarbons with formation of macromolecular carbon-chain compounds, we have investigated the polycondensation of 1,2-dichloroethane with chlorobenzene in presence of aluminum chloride. The purpose of the investigation was to determine the essential features of the polycondensation reaction between 1,2-dichloroethane and an aromatic hydrocarbon of reduced "functionality", as compared with unsubstituted benzene. The benzene molecule contains six hydrogen atoms that may be replaced with alkyl groups, and the products of the condensation of 1,2-dichloroethane with benzene may therefore have a branched structure, so that three-dimensional condensation products may be formed in which linear molecules of poly[ethylenephenyl] are cross-linked together.

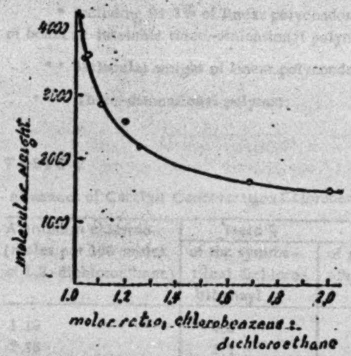


Fig. 1

It is known, however, that the introduction of two substituents into the benzene nucleus renders further alkylation difficult, so that it might be expected that the polycondensation of 1,2-dichloroethane with chlorobenzene would differ somewhat from the polycondensation of 1,2-dichloroethane with benzene, since in the former process a third substituent must enter the benzene nucleus. In order to elucidate the effect of the proportions of the reactants on the properties and yield of reaction products, a series of experiments was carried out in which the duration of the reaction and the amounts of chlorobenzene and aluminum chloride were maintained constant, but the amount of 1,2-dichloroethane was varied. The experimental procedure was the same as that used previously [2], with the exception that, after the solvent had been distilled off, only the symmetrical dichlorobibenzyl was distilled off under reduced pressure. The results are given in Table 1 and in Fig. 1. The molecular weights of the polycondensation products were determined viscosimetrically, K_m being taken as 1.8×10^{-4}.

Table 1 shows that reduction in the excess of chlorobenzene results in increased yield of macromolecular products and reduced yield of the symmetrical dichlorobibenzyl. Also, the molecular weight of the macromolecular polycondensation product, poly[(chloro)ethylenephenyl], rises as the excess of chlorobenzene is reduced, and reaches its highest value when the proportions of the reactants approximate to equimolecular, a fact that is in accord with the theory of linear polycondensation proposed by one of the present authors [4]. It is interesting to note that the formation of three-dimensional condensation products occurs only when the molar ratio of chlorobenzene to 1,2-dichloroethane is unity or less than unity (a 1% excess of chlorobenzene yields a mixture of linear condensation product and three-dimesional polymer), whereas three-dimensional products are formed in the polycondensation of 1,2-dichloroethane with benzene, even when there is a 20% excess of benzene [2]. This indicates that the introduction of a chlorine atom into the benzene nucleus hinders the formation of polycondensation products of branched structure and of the three-dimensional polymers formed from these by reaction among themselves and with linear condensation products.

It may therefore be considered as proved that the functionality of the benzene molecule is reduced by the replacement of a hydrogen by chlorine to a greater extent than would be expected simply on the basis of the reduction of the number of hydrogen atoms in the benzene nucleus. If, in fact the five hydrogens of chlorobenzene and the six hydrogens of benzene are equally prone to replacement by aliphatic connecting bridges, then the reduction of the functionality of benzene from 6 to 5 in chlorobenzene, and to 4 in disubstituted benzenes, should not have any appreciable effect on the tendency of these aromatic hydrocarbons to form branched and three-dimensional structures. However, the introduction of one chlorine atom into the benzene nucleus is sufficient to reduce the tendency to form three-dimensional structures to a very great extent, and the introduction of two substituents into the benzene nucleus has been shown, in an investigation carried out simultaneously with the one now described, to cause the aromatic hydrocarbon to behave as a bifunctional compound, despite the presence of four hydrogen atoms potentially able to be replaced. Hence, the practical, or reactional, functionality of chlorobenzene is less than its potential functionality [5].

TABLE 1

Polycondensation of 1,2-Dichloroethane with Chlorobenzene (Aluminumchloride : chlorobenzene = 0.1)

Molar ratio chlorobenzene : 1,2-dichloroethane	Yield (%)		Molecular weight of polymer
	of the symmetrical dichlorobibenzyl	of polymer	
2.0	21.6	57.9	1570
1.68	15.9	59.3	1720
1.25	8.3	74.1	2230
1.19	7.4	74.7	2580
1.095	5.5	74.8	2850
1.05	3.4	69.1	3640
1.035	3.10	61.3	3590
1.01	—	81.1 *	4250 * *
0.793	—	86.3 * * *	—
0.747	—	76.9 * * *	—

* Including 24.3% of linear polycondensation product and 56.8% of benzene-insoluble three-dimensional polymer.

** Molecular weight of linear polycondensation product.

*** Three-dimensional polymer.

TABLE 2

Influence of Catalyst Concentration Chlorobenzene-dichloroethane = 1.19

Aluminum chloride (moles per 100 moles of 1,2-dichloroethane)	Yield %		Molecular weight
	of the symmetrical dichlorobibenzyl	of poly[(chloro)ethylenephenyl]	
1.19	0.5	–	
2.38	1.7	68.7	2380
3.57	1.4	67.8	3050
4.74	7.7	70.9	2930
5.94	5.3	63.7	3180
7.14	4.6	72.5	2680
8.32	3.4	74.2	2850
9.56	2.4	82.1	2390
10.71	3.4	73.3	2700

It has already been shown, by two of the present authors and Smirnova [2,3], that the course of the polycondensation of 1,2-dichloroethane with benzene is determined not only by the proportions of the reactants, but also by the concentration of the catalyst. Since the part played by the catalyst concentration in polycondensation processes has not yet been fully elucidated, we considered it desirable to determine whether the regularities that we observed previously for the condensation of 1,2-dichloroethane with benzene are found also in the reaction of 1,2-dichloroethane with chlorobenzene. With this object in view, we carried out a series of experiments in which the duration of the reaction and the amounts of chlorobenzene and 1,2-dichloroethane remained constant, but the amount of aluminum chloride was varied. The experimental procedure was the same as in the first series of experiments. The results are given in Table 2 and Fig. 2.

Table 2 and Fig. 2 show that in the polycondensation of chlorobenzene with 1,2-dichloroethane in presence of aluminum chloride, as in the polycondensation of benzene with dichloroethane [3], the concentration of the catalyst is not a matter of indifference. At low aluminum chloride concentrations, no polycondensation products are formed. Increase in the concentration of catalyst results in the formation of macromolecular polycondensation products, and the molecular weight of these products increases with increase in catalyst concentration, but only up to a certain value of this concentration. Further increase in catalyst concentration leads to a reduction in the molecular weight of the poly[(chloro)ethylenephenyl] although the fall is not so marked as in the polycondensation of 1,2-dichloroethane with benzene [3].

Apart from this study of regularities to be observed in the polycondensation of 1,2-dichloroethane with chlorobenzene, we made an investigation of the structure of the products of this reaction. The product of lowest molecular weight to be expected from this reaction is one of the isomeric symmetrical dichlorobibenzyls:

$$2ClC_6H_5 + ClCH_2CH_2Cl \xrightarrow{AlCl_3} ClC_6H_4CH_2CH_2C_6H_4Cl + 2HCl$$

The product of low molecular weight that we obtained boiled at 163-164° (3 mm) after being distilled twice. It was a colorless liquid, which became very viscous when cooled but did not yield any crystals.

In order to determine the structure of this symmetrical dichlorobibenzyl, we subjected it to oxidation and obtained p-chlorobenzoic acid as the sole product. This indicated that the product was essentially 4,4'-dichlorobibenzyl. It is reported in the literature [6] that 4,4'-dichlorobibenzyl does not readily pass into the crystalline state, the translition never being complete, even after careful distillation and the selection of a narrow fraction.

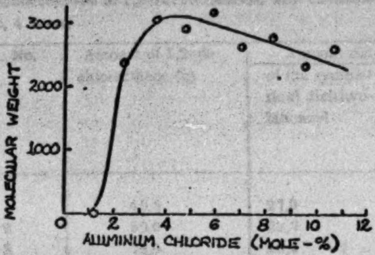


Fig. 2

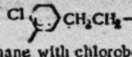
In order to determine the structure of the macromolecular polycondensation products, we submitted them to oxidative degradation, in the hope of obtaining a chlorobenzendicarboxylic acid, the identification of which would indicate the relative positions of the aliphatic bridges —CH_2CH_2— and the chlorine. Analysis of the polycondensation products showed that the composition of the repeating unit was —$C_6H_3ClCH_2CH_2$—.

However, we did not obtain a dicarboxylic acid when we oxidized the polycondensation products with chromic acid mixture. The main product was found to be p-chlorobenzoic acid, which we identified by its melting point, molecular weight (determined by titration with alkali), and elementary composition. After purification, the p-chlorobenzoic acid so obtained melted at 230-235°.

Oxidative degradation with potassium permanganate in acid, neutral, and alkaline media again did not yield a dicarboxylic acid. Hence, by oxidative degradation it was possible to determine the position of only one of the aliphatic connecting bridges with respect to the chlorine atom.

In an attempt to determine the structure of the polycondensation products we examined also their chemical degradation with benzene in presence of aluminum chloride. Two products could be expected as a result of this reaction: 4-chlorobibenzyl (on the basis of the results of oxidative degradation) and an isomeric chlorobibenzyl, the structure of which should indicate the position of the second aliphatic bridge. The products isolated from this degradation reaction were 4-chlorobibenzyl, identified by its melting point, and a very small amount of a liquid, which we did not succeed in identifying.

On the basis of these results we can make some suggestions concerning the structure of these products. It has been proved that the chlorine atom is in the para position to one of the —CH_2CH_2— bridges. From the absence of aromatic dicarboxylic acids in the oxidation products, it may be inferred that the second aliphatic bridge is probably in the position ortho to the chlorine. This supposition is based on the well known fact that the aromatic ring is readily destroyed during the oxidation of aromatic hydrocarbons having a substituent ortho to the aliphatic radical. In the oxidation of such compounds, either the ortho-substituted benzoic acid is not obtained at all, or it is obtained in extremely low yield. Also the orienting effects of the chlorine and the first aliphatic substituent favor the ortho-orientation of the second —CH_2CH_2—bridge. It is well known that in alkylation reactions in presence of aluminum chloride chlorine directs the entering substituent into the ortho and para positions, but an aliphatic residue directs the second aliphatic substituent into the meta position. Since the low-molecular-weight reaction product is 4,4'-dichlorobibenzyl, it may be assumed that the first aliphatic residue enters the position para to chlorine, and that the second residue then enters the position ortho to chlorine. It may therefore be assumed that the most probable elementary repeating unit is as follows:



so that the product of the polycondensation of 1,2-dichloroethane with chlorobenzene may be named poly [2-chloro-5-ethylenephenyl].

EXPERIMENTAL

The experimental procedure was the same as that described previously [2], with the exception that only the symmetrical dichlorobibenzyl was distilled off under reduced pressure (over the range 120-180° at 3 mm). The experimental conditions and the results obtained are given in Tables 3 and 4.

Oxidation of Polycondensation Products

Oxidation of the Symmetrical Dichlorobibenzyl. The symmetrical dichlorobibenzyl (10 g) was refluxed with nitric acid (280 ml; sp. gr. 1.1) for 10-11 hours. The mixture was then rendered alkaline with a 20-25% solution of caustic soda, and was boiled for 8-10 hours, during which time 18 g of potassium permanganate was added in 2-g portions. Excess of potassium permanganate was removed by addition of methanol, and the mixture was filtered at the pump. The filtrate was acidified to Congo red, and the precipitated acid was filtered off. After recrystallization from water, the acid melted at 217-218°.

Found %: M 145.4; 143.2

$C_7H_5O_2Cl$. Calculated %: M 156.6

TABLE 3

Polycondensation of 1,2-Dichloroethane with Chlorobenzene (Chlorobenzene, 112.6 g; aluminum chloride, 13.3 g; time, 4 hours)

Expt. No.	Amount of 1,2-dichloroethane (g)	Amount obtained (g)		Concentration of benzene solution of poly [(chloro)-ethylenephenyl] (g/100 ml)	Specific viscosity	Molecular weight of poly[(chloro)-ethylene-phenyl]
		of the symmetrical dichlorobibenzyl	of poly [(chloro)-ethylenephenyl]			
1	49.5	27.0	30	1.932	0.0405	1570
2	59.0	23.7	49	3.432	0.0768	1720
3	79.0	16.5	82	3.975	0.115	2230
4	83.2	15.5	87	3.336	0.112	2530
5	90.3	12.5	94.5	3.131	0.116	2850
6	94.3	8.0	91	3.482	0.165	3640
7	95.6	7.5	82	3.506	0.163	3590
8	93.0	–	111*	3.388***	0.187	4250
9	112.6	–	136**	–	–	–
10	132.5	–	142.5**	–	–	–

* 33.4 g of benzene-soluble polycondensation product and 77.6 g of benzene-insoluble three-dimensional polymer.

** Three-dimensional polymer.

*** For the soluble polycondensation product.

Analysis of the soluble polycondensation product

Found %: C 69.71; 69.66; H 5.04; .06; Cl 25.51; 25.41

C_8H_7Cl Calculated %: C 69.33, H 5.09; Cl 25.58

TABLE 4

Polycondensation of 1,2-Dichloroethane with Chlorobenzene (Chlorobenzene, 112.6 g; 1,2-dichloroethane, 83.2 g)

Expt. No.	Amount of aluminum chloride (g)	Amount obtained (g)		Concentration of benzene solution of poly [(chloro)ethylenephenyl] (g in 100 ml)	Specific viscosity	Molecular weight of poly[(chloro)-ethylenephenyl
		of the symmetrical dichlorobibenzyl	of poly[(chloro)ethylenephenyl]			
11	1.33	1.0	–	–	–	–
12	2.66	3.5	79.0	3.312	0.102	2380
13	3.99	3.0	78.0	3.476	0.138	3050
14	5.30	16.0	81.5	3.036	0.116	2930
15	6.65	11.0	73.2	3.833	0.158	3180
16	8.00	9.5	83.4	3.810	0.133	2680
17	9.31	7.0	85.4	3.474	0.142	2850
18	10.70	5.5	94.5	3.047	0.095	2390
19	12.00	7.1	84.3	4.993	0.175	2700

Oxidative Degradation of the Polycondensation Products. A mixture of 20 g of the product of the polycondensation of 1,2-dichloroethane with chlorobenzene, 200 g of potassium dichromate, 600 ml of water, and 150 g of sulfuric acid was boiled for 80 hours. The mixture was then poured into 2-3 times its volume of water, and the precipitate that formed was filtered off. The precipitate was treated with 10% ammonia solution, and the solution was filtered and acidified to Congo red. The precipitated acid was filtered off, washed with a little water, and dried in a vacuum desiccator. During the oxidation a white substance collected in the reflux condenser, and this was found to be identical with the substance isolated from the reaction mixture. After recrystallization from water, the acid melted at 230-235°.

Found %: C 53.85; 53.69; H 3.25; 3.28

$C_7H_5O_2Cl$ Calculated %: C 53.69 H 3.22

Degradation of the Polycondensation Products with Benzene

A mixture of 20 g of the product of the polycondensation of 1,2-dichloroethane with chlorobenzene (molecular weight 3150), 20 g of aluminum chloride, and 200 ml of benzene was prepared in a flask fitted with a reflux condenser. The mixture was boiled in a water bath for five hours. Decomposition was then effected with dilute hydrochloric acid, and the usual further treatment was given. Vacuum fractionation yielded 2 g of a fraction boiling over the range 150-200° (3 mm). This fraction solidified, and after recrystallization from alcohol it melted at 49°, which is the melting point of 4-chlorobibenzyl [7].

SUMMARY

1. The polycondensation of 1,2-dichloroethane with chlorobenzene has been studied and the essential features of the process have been established.

2. It has been found that the introduction of a chlorine atom into the benzene nucleus hinders the formation of three-dimensional polycondensation products.

3. The polycondensation product has been investigated, and views have been expressed relating to its structure.

LITERATURE CITED

[1] V. V. Korshak, G. S. Kolesnikov, and A. V. Kharchevnikova, Proc. Acad. Sci. USSR, 56, 169 (1947).

[2] G. S. Kolesnikov, V. V. Korshak, and T. V. Smirnova, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 5 596 (1951).

[3] G. S. Kolesnikov, V. V. Korshak, and T. V. Smirnova, Bull Acad. Sci. USSR, Div. Chem. Sci., No. 1 172, (1955). •

[4]. V. V. Korshak, Chemistry of Macromolecular Compounds, Acad. Sci. USSR Press, Moscow and Leningrad, (1950).

[5]. Methods of Macromolecular Organic Chemistry, Vol I: V. V. Korshak, General Methods for the Synthesis of Macromolecular Compounds, Acad. Sci. USSR Press, Moscow, p. 472. (1953).

[6]. H. Meyer, A. Hofmann, Monatsh. 38, 161 (1917); R. L. Datta, F. V. Fernandes, J. Am. Chem. Soc. 38, 1809. (1916).

[7]. F. Bergmann, J. Weizman, D Schapiro, J. org. Chem., 9, 408 (1944).

Received January 27, 1954

N. D. Zelinsky Institute of Organic Chemistry of the USSR Academy of Sciences

• Consultant's Bureau Translation, p. 151

BLANK
PAGE

MACROMOLECULAR COMPOUNDS

COMMUNICATION 72. FORMATION OF A THREE-DIMENSIONAL POLYMER BY REACTION OF POLY[ETHYLENEPHENYL] WITH DIHALOALKANES

V. V. Korshak, G. S. Kolesnikov, and T. A. Soboleva

Investigation of the transarylation reaction of bibenzyl [1], and also of the polycondensation of 1,2-dichloroethane with benzene [2, 3], has shown that at a definite stage of the reaction a three-dimensional product is formed as a result of the cross-linking of the chains of the linear polymer formed in the earlier part of the reaction. An examination of the results obtained has led two of the present authors to suggest that it is mainly the longest molecules that are concerned in the formation of a three-dimensional product in the transarylation of bibenzyl, so that the molecular weight of the poly[ethylenephenyl] remaining in solution is reduced [4].

Since the formation of three-dimensional polymers is of great interest as a process extensively applied in various branches of polymer chemistry, for example, in the vulcanization of rubber and the conversion of resol into resite, we have studied some of the features of this process, as shown in the reactions of poly[ethylenephenyl] with some dihaloalkanes. We have shown previously that the polycondensation of benzene with 1,2-dichloroethane, particularly when the latter is present in excess, results in the formation of three-dimensional products, which are insoluble in benzene and other solvents [2, 3]. It may be expected, therefore, that, by reaction with various dihaloalkanes in presence of aluminum chloride, poly [ethylenephenyl] will yield three-dimensional products as a result of the formation of cross links between linear poly[ethylenephenyl] molecules.

The original poly[ethylenephenyl] used throughout the investigation was an artificially prepared mixture of two samples of separately prepared poly[ethylenephenyl]; they were synthesized and purified in the way already described [2, 3]. The molecular weight, as determined from viscosity measurements on a 3% benzene solution, was 11,470 for the first sample, 2,140 for the second sample, and 5,930 for the mixture.

The following dihaloalkanes were used as cross-linking agents: dibromomethane, 1,2-dibromoethane, 1-bromo-3-chloropropane, 1,4-dibromobutane, and 1,6-dibromohexane. Bromo derivatives were used, rather than chloro derivatives, because their boiling points are higher and the losses during the reaction therefore lower.

The reactions of poly[ethylenephenyl] with these dihaloalkanes were carried out for various concentrations of the latter compounds. The catalyst was anhydrous aluminum chloride (0.9 mole per mole of dihaloalkane). The duration of the reaction and the temperature were the same in all experiments (three hours, 120°). After the reaction the mixture was treated with dilute hydrochloric acid, and then benzene. The insoluble three-dimensional polymer was filtered off and washed with benzene until completely free of benzene-soluble substances. The substance remaining on the filter was the three-dimensional polymer; it was dried and weighed. The soluble poly[ethylenephenyl] was separated from the benzene solution by distilling off the solvent, the residue being dried to constant weight. The results are given in Table 1.

The data in Table 1 show that, when poly[ethylenephenyl] is heated with a dihaloalkane in presence of anhydrous aluminum chloride, an insoluble three-dimensional product is formed in an amount that depends both on the identity of the dihaloalkane and the amount of this taken. The dihaloalkanes can be placed in the following order, corresponding to increasing yield of three-dimensional polymer from a given amount of the dihaloalkane: 1,4-dibromobutane, 1-bromo-3-chloropropane, 1,6-dibromohexane, dibromomethane, and 1,2-dibromoethane.

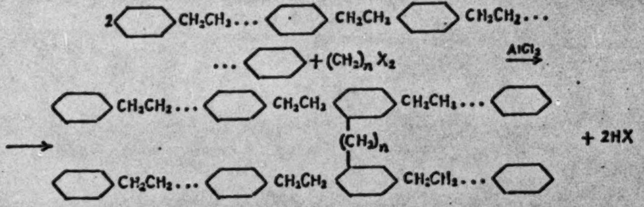
The least active of the cross-linking agents are 1,4-dibromobutane and 1-bromo-3-chloropropane, for they give the lowest yields of three-dimensional polymer. This fact must be associated with the tendency of these halo compounds to form tetrahydronaphthalene and indan derivatives with benzene and its homologs, which leads to a reduction in the amount of the dihalo compound available for cross-linking the poly[ethylenephenyl] and therefore a reduction in the yield of three-dimensional polymer. The remaining investigated dibromo compounds, owing to the operation of stereochemical factors, have no tendency to form rings, and they give higher yields of three-dimensional polymer. The yield of the latter is dependent also on the amount of cross-linking agent, as will be seen from the results given in Table 1. With increase in the amount of cross-linking agent, the yield of three-dimensional polymer rises in a regular manner in all cases.

TABLE 1

Reaction of Poly[ethylenephenyl] with Dihaloalkanes

Dihaloalkane	Amount of dihaloalkane per basic mole of poly[ethylenephenyl] (mole-%)	Amount obtained (% of original amount) of insoluble three-dimensional polymer	Amount obtained (% of original amount) of soluble poly[ethylenephenyl]	Molecular weight of the soluble poly[ethylenephenyl] isolated
Dibromomethane	2.15	16.4	83.4	6290
	6.45	15.3	82.6	5120
	8.60	20.0	80.5	3120
1,2-Dibromoethane	2.15	15.8	76.8	5610
	4.30	24.7	68.0	5700
	8.60	24.0	65.4	5580
	12.90	35.8	61.8	2230
1-Bromo-3-chloropropane	2.15	16.7	81.2	5400
	4.30	18.8	80.0	5170
	12.90	19.8	76.4	3110
1,4-Dibromobutane	2.15	4.9	84.6	6100
	6.45	6.7	79.3	5560
	8.60	9.8	71.4	5150
	12.90	15.6	81.6	4420
1,6-Dibromohexane	2.15	4.0	90.2	5810
	4.30	12.2	81.4	5110
	8.60	16.2	79.1	4670
	12.90	26.4	73.0	4110

The molecular weight of the poly[ethylenephenyl] that does not react is at first almost constant, and only when the amount of cross-linking agent exceeds 8 mole-% is there a noticeable fall in the molecular weight of the soluble polymer. It is clear from this behavior that the cross-linking reaction proceeds in two stages. In the first stage cross-linking occurs between a few (two, three, etc.) linear molecules:

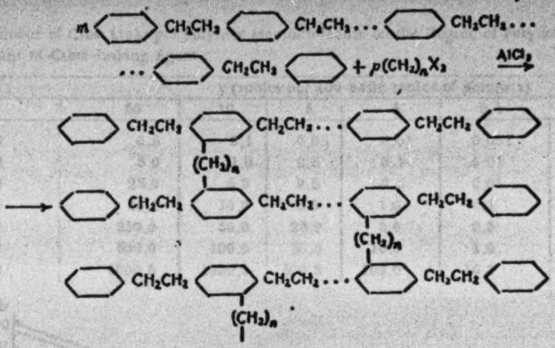

2 CH₂CH₂ ... CH₂CH₂ CH₂CH₂ ...
... + (CH₂)ₙX₂
AlCl₃
CH₂CH₂ ... CH₂CH₂ CH₂CH₂ ...
(CH₂)ₙ
+ 2HX
CH₂CH₂ ... CH₂CH₂ CH₂CH₂ ...

As a result of this, mainly branched molecules arise, and up to a certain degree of complexity they retain their solubility in benzene. The formation of such branched molecules will lead to an increased molecular weight, and this will compensate for the fall in molecular weight due to the higher tendency of the longer poly[ethylenephenyl] molecules to react.

Such branched molecules react further with formation of three-dimensional molecules, and so become insoluble in benzene This reaction can be represented as follows (see top of following page).

Thus, there is no difference in principle between branched and three-dimensional molecules. The difference lies only in the number of cross links and in the number of linear chains linked together.

As will be readily seen from the results given in Table 1, when the cross-linking agent is present in an amount of greater than 8%, there is a considerable fall in the molecular weight of the soluble poly[ethylenephenyl] that has not reacted. This fall in molecular weight is particularly great in the reaction with 1,2-dibromoethane; it is somewhat less for dibromomethane and 1-bromo-3-chloropropane, and still less for the remaining dibromo compounds. In the reaction with 1,2-dibromoethane, the residual soluble poly[ethylenephenyl] is almost free of the higher-molecular-



weight fraction, and consists almost entirely of the poly[ethylenephenyl] of lower molecular weight which was brought into the reaction as a component part of the original mixture. In this reaction, therefore, the high-molecular-weight component of the original mixture is converted almost completely into three-dimensional polymer. In the reactions with the other dihalo compounds, this feature is not so prominent, but the considerable fall in molecular weight, indicating the greater reactivity of the poly[ethylenephenyl] of higher molecular weight, is again quite obvious.

The original mixture of polymers consisted of ~ 60% low molecular weight (2140) and ~ 40% high molecular weight (11.470) (poly[ethylenephenyl]); whereas the poly[ethylenephenyl] isolated after the reaction with 1,2-dibromoethane in an amount equivalent to 61.8% of the whole of the original mixture had a molecular weight of 2230, that is to say, consisted in effect of the low-molecular-weight component of the original mixture, recovered practically without loss in an almost pure state. This great difference in the reactivities of poly[ethylenephenyl] preparations differing in molecular weight is determined by the variation with molecular weight of the probability of a polymer entering the reaction, as will be readily seen from the following considerations. Let $\underline{y}$ be the amount of the cross-linking agent (moles per 100 basic moles of polymer), $\underline{x}$ the degree of polymerization of the polymer, $\underline{a}$ the number of cross links per polymer macromolecule, and $\underline{b}$ the number of cross links per repeating unit, then:

$$b = \frac{y}{100}$$

and therefore

$$a = b \cdot x = \frac{y \cdot x}{100}$$

By the use of this equation it is easy to calculate the variation of the number of cross links formed between the macromolecules as a function of the degree of polymerization of the original polymer and of the amount of cross-linking agent, expressed as moles per 100 basic moles of the polymer. The results of this calculation are given in Table 2.

In Fig. 1 the number of cross links per repeating unit of the polymer is shown graphically in its dependence on the degree of polymerization for various amounts of cross-linking agent, expressed as moles per 100 basic moles of polymer. Fig. 1 shows how rapidly the number of cross links falls with increase in the degree of polymerization.

Increase in the amount of cross-linking agent results in a rapid increase in the number of cross links between the macromolecules, as can be readily seen from Fig. 2, which is constructed from the data in Table 2. It is again quite obvious that the magnitude of the molecular weight of the polymer plays an important part, and the number of cross links increases as the molecular weight — or its equivalent, the degree of polymerization — increases.

As the molecular weight, or degree of polymerization, increases, there is a sharp fall in the amount of cross-linking agent necessary for the formation of one cross link per polymer macromolecule, which is already sufficient for the conversion of the whole mass into one continuous macromolecule, i.e. for its conversion into a three-dimensional polymer. Fig. 3 shows the dependence of the amount of cross-linking agent necessary for the formation of one cross link per macromolecule on the degree of polymerization of the polymer that is being converted into a three-dimensional compound.

TABLE 2

Dependence of the Number of Cross Links per Polymer Macromolecule on the Degree of Polymerization of the Polymer and the Amount of Cross-linking Agent

x	y (moles per 100 basic moles of polymer)						
	100	50	10	5	1	0.1	0.01
1	1.0	0.5	0.1	0.05	0.01	0.001	0.0001
10	10.0	5.0	1.0	0.5	0.1	0.01	0.001
50	50.0	25.0	5.0	2.5	0.5	0.05	0.005
100	100.0	50.0	10.0	5.0	1.0	0.1	0.01
500	500.0	250.0	50.0	25.0	5.0	0.5	0.05
1,000	1000.0	500.0	100.0	50.0	10.0	1.0	0.1
10,000	10000.0	5000.0	1000.0	500.0	100.0	10.0	1.0

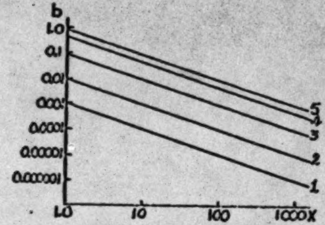


Fig. 1. Dependence of the number of cross links per repeating unit of polymer on the concentration of the cross-linking agent and on the molecular weight of the polymer: 1) $y' = 0.1$; 2) $y' = 1$; 3) $y' = 10$; 4) $y' = 50$; 5) $y' = 100$

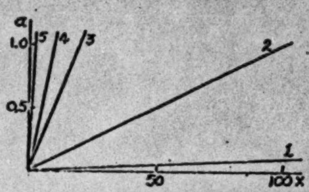


Fig. 2. Dependence of the number of cross links per macromolecule on the concentration of cross-linking agent and on the molecular weight of the polymer: 1) $y = 0.1$; 2) $y = 1$; 3) $y = 5$; 4) $y = 10$; 5) $y = 50$

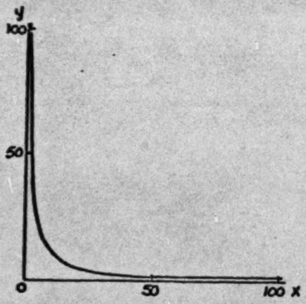


Fig. 3. Dependence of the concentration of cross-linking agent necessary for the formation of one cross link per macromolecule on the molecular weight of the polymer.

These considerations lead us to the conclusion that increase in the molecular weight of the polymer results in increased probability of reaction with cross-linking agent. Hence, when we have a mixture of molecules varying in size and subject it to the action of the cross-linking agent, the longer molecules are the first molecules to react. The molecules that react become cross-linked together, and at a definite stage of the process they are converted into the three-dimensional polymer. When the reaction conditions are such that the amount of cross-linking agent is insufficient to bring all of the molecules into the reaction and convert them into the three-dimensional polymer, the part of the linear polymer that does not react will include the shorter molecules. This conclusion, which has been derived theoretically, has been fully confirmed experimentally, as can be seen from the above-described results of the investigation of the reaction of poly-[ethylenephenyl] with dihalo compounds.

It is interesting to note the analogy that exists between the behavior of macromolecules of varying length in the cross-linking reaction discussed above and in degradation reactions, in which the longer molecules have been found in a number of cases to be more prone to attack. Thus, two of the present authors, in a study of the degradation of poly-[ethylenephenyl], have shown that degradation by means of benzene affects the longer molecules first [5]. One of us, in collaboration with Zamyatina [6], has made a similar observation for the degradation of polyamides with adipic acid or 1,6-hexanediamine. Similiar results were obtained also by one of the present authors, in collaboration with Golubev [7] and with Vinogradova [8], in a study of the degradation of polyesters by adipic acid or hexadecyl alcohol.

The theoretical basis of this peculiar feature of the chemical degradation of macromolecular compounds, treated on statistical principles, has been given by one of the present authors [9-14].

EXPERIMENTAL

The reactions between poly[ethylenephenyl] and dihalo compounds were carried out as follows. The polymer (5 g of a mixture of about 40% of poly[ethylenephenyl] of molecular weight 11,470 and 60% of poly-[ethylenephenyl] of molecular weight 2,140) was placed in a test tube, weighed amounts of the dihaloalkane and aluminum chloride were added, and the tube was closed with a stopper carrying a calcium chloride tube. The tube was then placed in a bath of Wood's metal and maintained at 120° with the aid of a contact thermometer and a relay.

TABLE 3

Experimental Conditions and Results for the Reaction of Poly[ethylenephenyl] with Dihaloalkanes

Dihaloalkane	Amount of dihaloalkane (g)	Amount of aluminum chloride (g)	Amount isolated after reaction, (g)		Properties of soluble poly-[ethylenephenyl]	
			of soluble poly-[ethylenephenyl]	of insoluble poly[ethylenephenyl]	Specific viscosity of a 3% solution in benzene	Molecular weight
Dibromomethane	0.18	0.12	4.172	0.882	0.327	6290
	0.54	0.38	4.132	0.765	0.266	5120
	0.72	0.50	4.025	1.001	0.162	3120
1,2-Dibromoethane	0.19	0.12	3.882	0.791	0.292	5610
	0.39	0.25	3.401	1.235	0.296	5700
	0.78	0.50	3.270	1.202	0.290	5580
	1.17	0.75	3.092.	1.790	0.116	2230
1-Bromo-3-chloro propane	0.16	0.12	4.062	0.940	0.281	5400
	0.32	0.25	4.001	0.835	0.269	5170
	0.96	0.75	3.820	0.992	0.162	3110
1,4-Dibromobutane	0.22	0.12	4.230	0.245	0.318	6100
	0.68	0.38	3.965	0.335	0.289	5560
	0.90	0.50	3.572	0.492	0.268	5150
	1.35	0.75	4.081	0.780	0.230	4420
1,6-Dibromohexane	0.25	0.12	4.512	0.202	0.302	5810
	0.50	0.25	4.070	0.610	0.266	5110
	1.00	0.50	3.955	1.321	0.243	4670
	1.50	0.75	3.651	0.819	0.214	4110

Heating of the reaction mixture was continued for three hours, and dilute hydrochloric acid and benzene were then added to the contents of the test tube. The liquid was poured into a flask, and the remainder of the contents of the tube were quantitatively transferred to the flask, with the aid of benzene as solvent. The mixture, which consisted of a benzene solution of poly[ethylenephenyl], an aqueous layer, and insoluble three-dimensional polymer, was filtered through a weighed sintered-base glass crucible, and the residue on the filter was washed with benzene until the benzene was no longer colored. The crucible and contents were dried to constant weight at 150-170°, and from its weight the amount of insoluble polymer was determined.

The benzene layer of the filtrate was separated in a separating funnel, washed with water until neutral, and dried with calcium chloride. The calcium chloride was filtered off and washed with dry benzene, the washings being added to the main filtrate. The greater part of the benzene was distilled off, and the residue was freed from benzene by heating it at 150-170° until a constant weight was attained.

The amounts of materials taken for reaction and the experimental results are given in Table 3.

SUMMARY

1. A study has been made of reactions, resulting in the formation of products of three-dimensional structure, which occur when poly[ethylenephenyl] is treated with various dihaloalkanes in presence of anhydrous aluminum

chloride.

2. It has been shown experimentally that, in the formation of three-dimensional products from an artificially prepared mixture of poly[ethylenephenyl] preparations differing in molecular weight, the three-dimensional polymer is built up mainly from the polymer components of higher molecular weight.

3. It has been shown that, in the conversion of a linear polymer into a three-dimensional polymer, the probability of a macromolecule becoming cross-linked increases as its molecular weight increases.

Received January 27, 1954.

N. D. Zelinsky Institute of Organic Chemistry of the USSR
Academy of Sciences

LITERATURE CITED

[1] V. V. Korshak and G. S. Kolesnikov, Proc. Acad. Sci. USSR, 70, 625 (1950).

[2] V. V. Korshak, G. S. Kolesnikov, and A. V. Kharchevnikova, Proc. Acad. Sci. USSR, 56, 169 (1947).

[3] G. S. Kolesnikov, V. V. Korshak, and T. V. Smirnova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1951, No. 5, 536.

[4] G. S. Kolesnikov and V. V. Korshak, in Collection "Problems of the Mechanism of Organic Reactions", Acad. Sci. UkrSSR Press, Kiev, 1953.

[5] G. S. Kolesnikov, V. V. Korshak, and T. V. Smirnova, in Collection "Chemistry and Physical Chemistry of Macromolecular Compounds", Acad. Sci. USSR Press, Moscow, 1952, p. 44.*

[6] V. V. Korshak and V. A. Zamyatina, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1945, No. 6, 609.

[7] V. V. Korshak and V. V. Golubev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1949, No. 4, 379.

[8] V. V. Korshak and S. V. Vinogradova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1951, No. 6, 756.

[9] V. V. Korshak, Proc. Acad. Sci. USSR, 64, 525 (1949); Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 5 (1950)

[10] V. V. Korshak, S. R. Rafikov, and V. A. Zamyatina, in Collection "Investigations on Macromolecular Compounds", Acad. Sci. USSR Press, Moscow and Leningrad, 1949, p. 7.

[11] V. V. Korshak, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1951, No. 6, 753.

[12] V. V. Korshak, Chemistry of Macromolecular Compounds, Acad. Sci. USSR Press, Moscow, 1950, p. 307.

[13] V. V. Korshak, Prog. Chem., 21, 146 (1952).

[14] Methods of Macromolecular Organic Chemistry, Vol. 1: V. V. Korshak, General Methods for the Synthesis of Macromolecular Compounds, Acad. Sci. USSR Press, Moscow, 1953, p. 495.

---

* Consultant's Bureau Translation, p. 45.

MACROMOLECULAR COMPOUNDS

COMMUNICATION 73. SOME TWO-COMPONENT MIXED POLYAMIDES

V. V. Korshak and T. M. Frunze

In a previous communication we have described mixed polyamides formed from 1,6-hexanediamine salts of two of the following acids: succinic, adipic, suberic, azelaic, and sebacic [1].

Investigation showed that there is a definite relationship between the properties of a mixed polyamide obtained in this way and the proportions of the reactants. Mixed polyamides have lower melting points than either of the polyamides obtained from the single component salts. For each of the investigated series of polyamides, the minimum melting point corresponds to the polymer containing 60 mole-% of the acid having the higher number of methylene groups. It was found also that there is a linear relationship between the melting points of polyamides and the content of amide linkages in the macromolecular chain. This relationship enabled us to calculate the proportion of amide groupings that are unable, for purely stereochemical reasons, to form hydrogen bonds, it being to the existence of such groupings that we must attribute the lower melting points, and higher solubilities in organic solvents of mixed polyamides, as compared with straight polyamides prepared from one salt.

It would be very interesting to determine the extent to which these relationships remain valid when one of the salts is replaced by an amino acid. With this object we have investigated series of mixed polyamides derived from 6-caprolactam (2-oxohexamethylenimine) and 1,6-hexanediamine salts of adipic, azelaic, and sebacic acids. Of these series, that derived from 1,6-hexanediamine adipate and 6-caprolactam has been investigated by Catlin, Czerwin, and Willey [2], and the melting point curve that we have obtained for this series is in accord with that given by these investigators.

EXPERIMENTAL

The reactions were carried out by the procedure described previously [1]. The mixture of reactants was heated in test tubes for six hours in an atmosphere of nitrogen carefully purified from oxygen in the temperature range 200-250° (30 minutes at 200°, 30 minutes at 220°, and five hours at 250°).

Starting Materials.

The original dicarboxylic acids were purified by recrystallizing them at least twice from water. In the first recrystallizations of azelaic and sebacic acids, a little potassium permanganate was added to oxidize oily impurities. The degree of purity of the acids was checked by titration to phenolphthalein with 0.02 N NaOH. The melting points of the acids used in the experiments were: adipic 152.5° (reported value 153° [3]), azelaic 106° (reported value 106.5° [4]), and sebacic 134° (reported value 134.5° [5]).

1,6-Hexanediamine was purified by two distillations under a reduced pressure of nitrogen; 5-10% of caustic soda or 5% of sodium was added to the diamine – this addition increases the loss of diamine, but a purer product is obtained. The distillate of liquid diamine was collected in a receiver cooled with a mixture of snow and salt; rapid cooling and solidification of the diamine makes it possible to obtain a much purer product that that obtained when the diamine remains for some considerable time in the molten state. The diamine obtained in this way can be preserved for a long time unchanged. It melted at 42° and boiled at 100° (20 mm) (the reported melting point is 42° [6]). The 6-caprolactam was purified by distillation, and it then melted at 68° (the reported melting point is 68-70° [7]).

One of the present authors has shown, in collaboration with Rafikov [8] and Golubev [9], that the molecular weight of a polyamide obtained by the polycondensation of a diamine with a dicarboxylic acid is reduced greatly when an excess of diamine or dicarboxylic acid is present. Polyamides of the highest molecular weights, therefore, may be prepared only when strictly equivalent amounts of diamine and dicarboxylic acid are used. The simplest and most reliable method of ensuring that the reactants are applied in equimolecular proportions is the use of previously prepared neutral salts, for all dicarboxylic acids, apart from oxalic, readily form neutral salts with 1,6-hexanediamine [10].

For the preparation of the salts a weighed amount of the acid was dissolved in hot 80% ethanol. A 5% excess of 1,6-hexanediamine – molten or, better, as a solution in 80% ethanol – was carefully added to the resulting hot solution (with stirring to avoid boiling over), and the boiling solution of the salt was rapidly filtered through a glass filter and allowed to cool. The salt that crystallized out was filtered off at the pump and recrystallized from 80% ethanol. The crystals were filtered off and rapidly washed on the filter with 96% ethanol; they were then drained under suction as efficiently as possible, and dried in the air. Rapid washing is essential, for if it is prolonged, diamine is extracted and an acid salt is obtained. Also, it is essential to drain the salt as thoroughly as possible to remove alcohol used for washing, for if alcohol remains in the salt, the latter is oxidized during drying in the air. Alcoholic solutions of the salts also oxidize very readily, and it is not recommended that they be left overnight. The total amount of solvent used in the preparation of the salts is 500 ml for 200 g of the original acid and 500 ml for 300 g of crude salt in the second crystallization.

When the alcohol used is more dilute, more of the salt is lost, for it is more soluble in water than in alcohol. When 95% ethanol is used, the salt obtained is yellowish, probably owing to the greater ease with which such solutions undergo oxidation in the air. The excess of free acid in the salts was determined by titration to phenolphthalein with 0.02 N NaOH. The salt used must be neutral.

The salts used for the reactions were: 1,6-hexanediamine adipate (AdH), m.p. 190.8-191°, 1,6-hexanediamine sebacate (SH), m.p. 174°, and 1,6-hexanediamine azelaate (AzH), containing two molecules of water of crystallization and melting at 102° in a sealed capillary. Anhydrous 1,6-hexanediamine azelaate, m.p. 148°, can also be prepared.

RESULTS

The mixed polamides that we prepared contained residues of 6-aminohexanoic acid, 1,6-hexanediamine, and one of the following dicarboxylic acids: adipic, azelaic, and sebacic. The proportions of these residues varied according to the proportions of the substances taken for the preparation of the samples. The melting points of the products were determined by the method described previously [1], and their solubilities in alcohol and other solvents were measured. The viscosities of 0.5% solutions of the products in cresol were determined; the mean molecular weight of the products was about 15,000. The results obtained are given in the table.

TABLE
Melting Points of Mixed Polyamides

Molar ratio of starting materials**	Original substances*		
	AdH/C	AzH/C	SH/C
1/0	250-252	205-208	210-212
0.8/0.2	220-225	180-187	195-200
0.6/0.4	190-196	155-160	178-185
0.5/0.5	180-190	135-140	170-174
0.4/0.6	170-177	130-135	160-165
0.2/0.8	165-173	135-140	153-158
0.1/0.9	174-177	175-178	160-168
0/1	215-217	215-217	215-217

* Abbreviations: Ad - adipic acid; Az - azelaic acid; S - sebacic acid: H - 1,6-hexanediamine: C - 6-caprolactam

** The numerator and denominator of each ratio refer to the substances in the numerator and denominator respectively at the top of each column under the heading "Original substances".

DISCUSSION OF RESULTS

Figures 1,2, and 3 show the variation in melting point with composition in the binary polymer systems studied.

These figures show that variation in the composition of the polymers is accompanied by variation in melting point and other properties. The melting points of mixed polyamides are lower than those of polyamides obtained from one component only. As the amount of the second component increases, the melting point falls and passes through a minimum corresponding to a product containing 6-caprolactam at a mole fraction of 0.8. It is interesting to note that this corresponds to about 60% by weight of caprolactam in the product, i.e. approximately the same proportion as we found for mixed polyamides obtained from salts of two dicarboxylic acids, for which the minimum melting point again corresponds to the product containing about 60% by weight of one of the components in its molecule [1].

For every series of polymers studied the minimum melting point is different, the lowest being found to be 130° for the AzH-C series, whereas for the AdH-C series it is 165°, and for the SH-C series it is 153°. Comparison of the series based on adipic and sebacic acids indicates that increase in the chain length of the dicarboxylic acid results in a lowering of the minimum melting point, but there are anomalies when the acid has an odd number of carbon atoms in its molecule, as can be seen from the behavior of the azelaic series, which has the lowest minimum melting point. As we have already shown [1], this can be explained by the reduced possibility of hydrogen-bond formation in polyamides derived from odd acids.

All of the polyamides that we have prepared are readily soluble in cresol, and many of them are dissolved when heated with ethanol or 2-methoxyethanol – with some difficulty, also 2-ethoxyethanol–but when cooled, these solutions immediately gelatinize. None of them is soluble in cyclohexanone, chloroform, or benzene. The most soluble products are those of the AzH-C series, and this series is followed by SH-C and AdH-C. Within each series, the product of lowest melting point has the highest solubility.

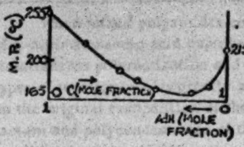


Fig. 1.

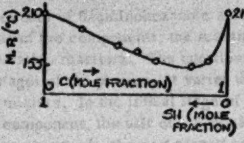


Fig. 2.

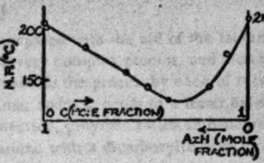


Fig. 3.

The variations in the properties of the investigated polyamides can be explained on the basis of the possibility of the formation of a greater or lower number of hydrogen bonds. A polyamide can be regarded as a polyethylene system in which, in addition to methylene groups, there are amide groupings, which, by forming hydrogen bonds, cause a raising of melting point and increase in mechanical strength which are directly proportional, to a first approximation, to the proportion of hydrogen bonds [1].

In mixed polyamides, not all of the amide groupings are able to form strong hydrogen bonds, owing to the operation of purely steric factors, which make it impossible for approaches to a distance of about 2.7 A to be made. For this reason, the presence of a certain number of amide groupings will affect the properties of a polyamide only to the extent to which these amide groupings can form hydrogen bonds with similar groupings in neighboring polyamide molecules. It may be noted in passing that, according to Mikhailov's results [11], the formation of intramolecular hydrogen bonds does not affect the melting point, but reduces the mechanical strength.

As will be seen from the scheme given below, in the mixed polyamide derived from the salt AdH and caprolactam taken in the proportions of 2 : 3, not all amide groupings are able to form hydrogen bonds:

```
−C−Ad−H−C−Ad−H−C−
−C−C−Ad−H−C−Ad−H−
−C−C−C−Ad−H−Ad−H−
```

If we represent the hydrogen bonds between amide groupings by dotted lines and indicate the number of atoms in each residue in the main chain of the mixed polyamide, we obtain the following picture:

```
−7−6−8−7−6−8−7−
 :       :   :
 :       :   :
−7−7−6−8−7−6−8−
 :     : : :
 :     : : :
−7−7−7−6−8−6−8−
```

It will be seen from this scheme that a considerable proportion of the amide groupings cannot form hydrogen bonds with amide groupings in neighboring molecules. This is the cause of the depressed melting points and enhanced solubilities of mixed polyamides.

For comparison, we give schemes for the formation of hydrogen bonds between amide groupings in straight polyamides, namely, the polyamide derived from the salt AdH (I) and that derived from caprolactam (II):

```
−6−8−6−8−6−8−6−8−      −7−7−7−7−7−7−7−7−7−
 : : : : : : : : :      :   :   :   :   :
 : : : : : : : : :      :   :   :   :   :
−6−8−6−8−6−8−6−8−      −7−7−7−7−7−7−7−7−7−
 : : : : : : : : :      :   :   :   :   :
 : : : : : : : : :      :   :   :   :   :
−6−8−6−8−6−8−6−8−      −7−7−7−7−7−7−7−7−7−

       (I)                    (II)
```

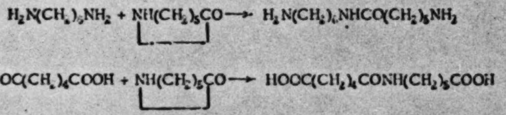
It can be readily seen that in straight polyamides the number of hydrogen bonds formed between the macromolecule chains will be very much greater than in mixed polyamides. It is interesting to note the great difference in the number of hydrogen bonds between the straight polymers derived from the salt AdH and from caprolactam; here, evidently, lies the cause of the considerable difference in melting point between poly[1,6-hexanediamine adipate] (I, m.p. 250°) and polycaprolactam (II, m.p. 215°).

Reaction Mechanism for the Formation of Mixed Polyamides

When mixed polyamides containing residues of 6-aminohexanoic acid are prepared with the aid of the lactam of 6-aminohexanoic acid caprolactam as one of the components, the reaction is a very complex process, and includes simultaneous polymerization and polycondensation reactions. The contribution made to the process by each of these types of reactions varies greatly at various stages of the process: it varies with time, and it depends to a lesser extent on the original composition of the reaction mixture. In the initial stage of the reaction, polymerization of 6-caprolactam and polycondensation of the second component, the salt of 1,6-hexanediamine with a dicarboxylic acid, proceed simulataneously. However, as the process proceeds, the part played by the polymerization reaction becomes less and less significant, owing to the exhaustion of the caprolactam, whereas the role of the polycondensation reaction becomes more and more important, and is ultimately predominant.

It is known [12] that the polymerization of 6-caprolactam proceeds in presence of water [13], acids [14], amines, alcohols, and other substances containing mobile hydrogen atoms [15] and is a special case of "hydrolytic" polymerization, the term proposed for the polymerization of cyclic lactams, cyclic esters, aldehydes, ketones, and other compounds of this type [16-19], as distinct from the polymerization of unsaturated compounds, which proceeds, according to the stucture of the monomer and the mode of initiation, as "radical" or as "ionic" polymerization [19].

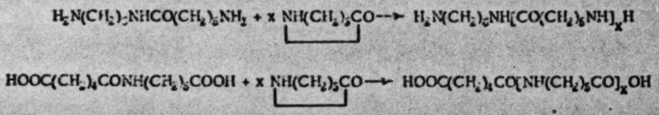
An example of hydrolytic polymerization is the polymerization of 6-caprolactam, which, in the processes dealt with in this paper, occurs in presence of an activator, namely, the 1,6-hexanediamine dicarboxylic acid salt added as second component. Each of the components forming the salt is capable of bringing about the polymerization of 6-caprolactam, chain growth being initiated according to the following scheme:



$$H_2N(CH_2)_6NH_2 + \underbrace{NH(CH_2)_5CO} \rightarrow H_2N(CH_2)_6NHCO(CH_2)_5NH_2$$

$$HOOC(CH_2)_4COOH + \underbrace{NH(CH_2)_5CO} \rightarrow HOOC(CH_2)_4CONH(CH_2)_5COOH$$

The resulting addition compound formed between the activator and the 6-caprolactam molecule enters into reaction with further caprolactam molecules, with formation of a polymer molecule according to the scheme:

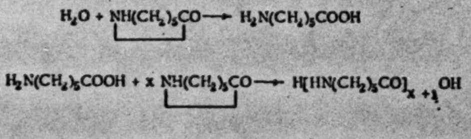


$$H_2N(CH_2)_6NHCO(CH_2)_5NH_2 + x\,\underbrace{NH(CH_2)_5CO} \rightarrow H_2N(CH_2)_6NH[CO(CH_2)_5NH]_xH$$

$$HOOC(CH_2)_4CONH(CH_2)_5COOH + x\,\underbrace{NH(CH_2)_5CO} \rightarrow HOOC(CH_2)_4CO[NH(CH_2)_5CO]_xOH$$

An interesting feature of the polymer so formed is the presence of terminal groupings consisting of residues of the activator used for the polymerization of the 6-caprolactam.

Also, water is formed in the polycondensation of the dicarboxylic acid salt of 1,6-hexanediamine, and in the first stage of the process this leads to the formation of 6-aminohexanoic acid, which reacts further in accordance with the above scheme, with formation of polycaprolactam:



$$H_2O + \underbrace{NH(CH_2)_5CO} \rightarrow H_2N(CH_2)_5COOH$$

$$H_2N(CH_2)_5COOH + x\,\underbrace{NH(CH_2)_5CO} \rightarrow H[HN(CH_2)_5CO]_{x+1}OH$$

However, the part played by water-initiated polymerization in the reactions we have investigated is evidently not great, for water vapor will be removed rapidly by the current of nitrogen passing through the reaction vessel.

The second component in the preparation of mixed polyamides (in our experiments this was the 1,6-hexanediamine salt of adipic, azelaic, or sebacic acid) can form a polymer only by a polycondensation reaction, which proceeds according to the equation:

$$xH_2N(CH_2)_6NH_2 + x\,HOOC(CH_2)_4COOH \rightarrow H[NH(CH_2)_6NHCO(CH_2)_4CO]_xOH + (2x-1)\,H_2O.$$

One of the present authors, with Rafikov [20], has shown that a factor favoring the polycondensation of the salts of diamines with dicarboxylic acids is their linear structure. An investigation of 1,6-hexanediamine adipate has shown that it has a linear structure [20]. Other workers have also expressed a similar opinion about the structure of these salts [21-24]. Shpitalny, Meos, and Koretskaya [25] have recently suggested the possibility of a cyclic structure for salts of diamines with dicarboxylic acids, but in the complete absence of any experimental support for this suggestion, it cannot be regarded as proved.

The main difference in principle between polymerization and polycondensation is that, in the first reaction, there is separation of a product of low molecular weight (water, alcohol, etc.), whereas in the second, no such product is formed; this difference is determined by the nature of the original reacting substances. The products of the polymerization of 6-caprolactam have certain peculiarities, in that they have functional groups – amino and carboxyl – at the ends of their macromolecules, and these are able to react with one another and with similar groups in other molecules.

At any stage of the process, therefore, polymers of 6-caprolactam are able to undergo polycondensation among themselves, with molecules of the 1,6-hexanediamine salt of the dicarboxylic acid, and with polyamides formed by the polycondensation of this salt. It is this polycondensation process, together with exchange reactions that we shall consider later, which is mainly responsible for the formation of a mixed polyamide, rather than a mixture of two polyamides, as the final product of the reaction.

One of the present authors, working with Bresler, Pavlova, and Finogenov [26], has made a detailed investigation of the mixed polyamide obtained by the polycondensation of a mixture of 20% of the salt SH, 40% of the salt AdH, and 40% of 6-caprolactam. Fractionation of this polyamide showed that it is a mixed polyamide, and not a mixture of various polyamides. Investigation of the molecular weight distribution function for this polyamide with the aid of the ultracentrifuge showed that this product was completely homogeneous.

The homogeneity in composition of mixed polyamides is determined also by the occurrence of exchange reactions, which result in a "leveling out" of the compositions of the macromolecules formed. Thus, in the same investigation [26] it was shown that heating of a mixture of two polyamide fractions differing in molecular weight resulted in the formation of a polyamide having an intermediate molecular weight corresponding to a state of polycondensation equilibrium under the given conditions. The great importance of exchange reactions in the polycondensation process, as a factor determining the leveling out of the compositions of the macromolecules formed, has been shown for a large number of other examples of the polycondensation reaction [27-29].

The tendency for polyamide macromolecules to react with one another with participation of the terminal amino and carboxyl groups must be fairly high, judging from the results of one of the present authors and Vinogradova [30] on the polycondensation of dicarboxylic acids with glycols, in which the main reaction leading to the formation of macromolecular polyesters was found to be the interaction between polyester molecules. The high reactivities of the macromolecules of polyurethans was shown by one of us and Gribova [31] in a study of the heteropolymerization of diisocyanates with glycols.

On the basis of these results it may be supposed that in polyamide formation the main way in which large macromolecules are formed is by the interaction of already formed polyamide macromolecules. Hence, in the formation of mixed polyamides, the last stage will be the polycondensation of polyamide macromolecules of various lengths with one another, and the very longest macromolecules, being much beyond the average size, will have the greatest tendency to undergo breakdown in degradative reactions, so that, in accord with actual observations [26], a polymer of low polydispersity will be formed.

SUMMARY

1. A study has been made of mixed binary polyamides formed from 6-caprolactam and a salt of 1,6-hexanediamine with adipic, azelaic, or sebacic acid.

2. It has been found that each of these series of polyamides has a minimum melting point when the mole percentage of 6-caprolactam is 80.

3. A reaction mechanism has been proposed for the formation of mixed polyamides from components that include 6-caprolactam.

LITERATURE CITED

[1] V. V. Korshak and T. M. Frunze, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, No. 1, 163.*

---

* See Consultants Bureau Translation, p. 143

[2] W. E. Catlin, E. P. Czerwin, R. N. Willey, J. Polymer Science 2, 412 (1947)

[3] G. Ciamician, P. Silber, Ber. 29, 485 (1896).

[4] C. Harries, C. Thieme, Ann. 343, 360 (1905).

[5] Voerman, Rec. trav. chim. Pays-Bas 23, 272 (1904).

[6] Th. Curtius, H. Clemme, J. prak. Chem. 62, 192 (1900).

[7] O. Wallach, Ann. 313, 345 (1900).

[8] V. V. Korshak and S. R. Rafikov, Proc. Acad. Sci. USSR, 48, 36 (1945).

[9] V. V. Korshak and V. V. Golubev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1946, 186.

[10] V. V. Korshak and S. R. Rafikov, J. Gen. Chem., 14, 974 (1944).

[11] N. V. Mikhailov, M. V. Nechaeva, and V. O. Klessman, In the Collection "Chemistry and Physical Chemistry of Macromolecular Compounds", Acad. Sci. USSR Press, Moscow, 1952, p. 265.

[12] Z. A. Rogovin, Chemistry and Technology of Artificial Fibers, State Light Ind. Press, Moscow, 1952, p. 622.

[13] I. L. Knunyants, Z. A. Rogovin, Yu. Rymashevskaya, and E. Khait, J. Gen. Ghem., 17, 987 (1947).

[14] V. V. Golubev, Candidate's Thesis, Inst. Org. Chem. Acad. Sci. USSR, 1947.

[15] V. V. Korshak, Chemistry of Macromolecular Compounds, Acad. Sci. USSR Press, Moscow and Leningrad, 1950, p. 231

[16] V. V. Korshak and N. G Matveeva, Proc. Acad. Sci. USSR, 78, 1145 (1951).

[17] V. V. Korshak and N. G. Matveeva, J. Gen. Chem., 22, 1173 (1952).*

[18] V. V. Korshak, I. A. Gribova, and N. G. Matveeva, Prog. Chem., 21, 134 (1952).

[19] V. V. Korshak, Methods of Macromolecular Organic Chemistry, Vol. 1, General Methods for the Synthesis of Macromolecular Compounds, Acad. Sci. USSR Press, Moscow, 1953, p. 184.

[20] S. R. Rafikov and V. V. Korshak, Bull Acad. Sci. USSR, Div. Chem. Sci., 1944, 432.

[21] T. Lieser, H. Gehlen, M. Gehlen-Keller, Ann. 556, 114 (1944).

[22] R. Brill, Naturwiss. 29, 220 (1941).

[23] W. H. Carothers, U. S. Pat. 2130947; Chem. Abs., 32, 9497 (1938).

[24] F. Sommer, K. Weise, Z. anorg. Chem. 94, 79 (1916).

[25] A. S. Shpitalny, E. A. Meos, and A. I. Koretskaya, J. Gen. Chem., 20, 571 (1950).**

[26] S. E. Bresler, S. A. Pavlova, and P. A. Finogenov, Proc. Acad. Sci. USSR., 87,961 (1952).

[27] V. V. Korshak, G. N. Chelnokova, and G. I. Distler, Proc. Acad. Sci. USSR, 82, 589 (1952).

[28] V. V. Korshak and S. V. Vinogradova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1952, 1109.***

[29] V. V. Korshak, Prog. Chem., 21,121 (1952).

[30] V. V. Korshak and S. V. Vinogradova, Proc. Acad. Sci. USSR, 77, 277 (1951).

[31] V. V. Korshak and I. A. Gribova, Proc. Acad. Sci. USSR, 82, 397 (1952).

Received February 10, 1954

N. D. Zelinsky Institute of Organic Chemistry of the
USSR Academy of Sciences

---

* See Consultants Bureau Translation, p.1221

** See Consultants Bureau Translation, p. 603

*** See Consultants Bureau Translation, p. 967

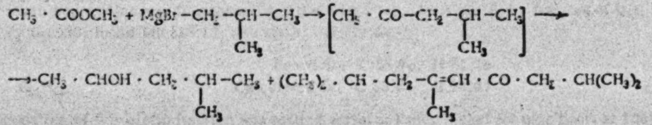
BRIEF COMMUNICATIONS

REACTION OF 2-METHYLALLYLMAGNESIUM CHLORIDE WITH ESTERS OF PALMITIC AND 2-ETHYLHEXANOIC ACIDS

A. D. Petrov, V. M. Melekhin, and A. M. Nefedov

In a series of investigations Petrov and coworkers [1] have shown that tert-alkylmagnesium halides (tert-butylmagnesium chloride) react with esters of monobasic aliphatic acids in accordance with the so-called "anomalous" scheme, with formation of ketones of the type R · CO · R, though acids of low molecular weight also give ketones of type R · CO · R' and their reduction products – the secondary alcohols R · CHOH · R'.

Isobutylmagnesium halides also react anomalously with esters of monobasic acids. As Shine and Turner showed [2], even methyl acetate reacts with $MgBrCH_2 \cdot \underset{\displaystyle CH_3}{\underset{|}{C}}H-CH_3$ according to the scheme:



$$CH_3 \cdot COOCH_3 + MgBr-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}H-CH_3 \rightarrow \left[CH_3 \cdot CO-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}H-CH_3\right] \longrightarrow$$

$$\longrightarrow CH_3 \cdot CHOH \cdot CH_2 \cdot \underset{\displaystyle CH_3}{\underset{|}{C}}H-CH_3 + (CH_3)_2 \cdot CH \cdot CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH \cdot CO \cdot CH_2 \cdot CH(CH_3)_2$$

i.e. with formation of both the secondary alcohol R · CHOH · R' and the product of the dehydrational condensation of the ketone R · CO · R'.

Grignard reagents derived from compounds of the allyl halide type have already been widely studied in Grignard-Wurtz reactions, and the extensive material now available shows that their use in place of the corresponding saturated compounds removes so-called steric hindrance and considerably increases the yields of hydrocarbons of the desired skeleton [3]. However, the reactions of carbonyl compounds (ketones and esters) with alkenyl magnesium halides having a double bond in the β-position have received almost no study at all, though it may be predicted that these reagents will react mainly by the "normal" scheme with the formation of much smaller amounts of "anomalous" reaction products. The present work was carried out with the object of filling this gap. It has been established that methyl palmitate reacts will 2-methylallylmagnesium chloride mainly according to the normal scheme, a 56% yield of 2-methyl-4-(2-methylallyl)-1-nonadecen-4-ol being formed (the yield of palmitone (16-hentriacontanone), formed by the anomalous scheme, was only 8%). When as ester of lower molecular weight – methyl 2-ethylhexanoate – was used, the corresponding tertiary alcohol was obtained in 80% yield, and no anomalous products were isolated. The alcohols obtained were hydrogenated to the saturated tertiary alcohols, the products were dehydrated to olefins, and the olefins were hydrogenated to paraffin hydrocarbons, namely, 4-isobutyl-2-methylnonadecane (freezing at -10° to a crystalline solid) and 5-ethyl-4-isobutyl-2-methylnonane (freezing to a glass at -90°).

EXPERIMENTAL

2-Methyl-4-(2-methylallyl)-1-nonadecen-4-ol. In accordance with Yarovsky's method, a mixture of 453.5 g (1.68 moles) of methyl palmitate and 350 g (3.8 moles) of 2-methylallyl chloride dissolved in 1200 ml of ether was added, under stirring, to 125 g (5.14 moles) of magnesium in 700 ml of ether. After being heated for 36 hours, the mixture was decomposed, the ether layer was separated, and the ether was distilled off. The reaction products were separated by vacuum fractionation, and 165 g (0.61 mole) of unchanged methyl palmitate, boiling at 146-156° (3 mm) and melting at 30°, was obtained, and also 210 g of a fraction boiling at 200° (3 mm) (56% yield on the amount of methyl palmitate that reacted). This substance had n_D^{20} 1.4615; d_4^{20} 0.8582; Kaufmann bromine number 89.96 (calculated 91.27); OH content by the Tserevitinov reaction 5.04% (calculated for $C_{24}H_{46}O$ 4.85%). This tertiary alcohol readily gave a carbanilic ester (phenylurethan) in the cold; it melted at 89.5°.

Found %: C 79.82; H 11.23
$C_{31}H_{51}NO_2$. Calculated %: C 79.26; H 10.94

When the tertiary alcohol was distilled, a solid residue (18 g) remained in the flask; it melted at 82°.

Found %: C 82.98; H 13.83

$C_{31}H_{62}O$. Calculated %: C 82.59; H 13.86

Its oxime was prepared and was found to melt at 58.5°.

2-Isobutyl-2-methylnonadecane. 2-Methyl-4-(2-methylallyl)-1-nonadecen-4-ol (50 g) was dissolved in 150 ml of methanol and hydrogenated over Raney nickel in an autoclave, first at room temperature and 130 atm, and then at about 150°. After 20 hours the autoclave was cooled and the methanol was distilled off. 2-Isobutyl-2-methyl-4-nonadecanol was found to have the following properties: b.p. 196° (2 mm), n_D^{20} 1.4515; d_4^{20} 0.8413.

Landa [4] has dehydrated similar tertiary alcohols (3-ethyl-3-octadecanol and others) by heating them with zinc chloride at about 120°. Examination of the oxidation products of the resulting substances showed that dehydration occurred preferentially in the smaller of the radicals at the tertiary carbon. No isomeric changes were observed. Nevertheless, we attempted to effect the dehydration by Hickinbottom's method [5], namely, heating at 150° with acetic anhydride and sodium acetate. However, even when heating was prolonged for 60 hours, less than one-third of the compound had undergone dehydration, i.e. the method appeared to be unsuitable for alcohols of high molecular weight.

We then decided to prepare the olefin by pyrolysis, not of the acetic ester of the alcohol, but of its ester with an acid of higher molecular weight, namely, 2-ethylhexanoic acid. It was found, however, that already in the process of preparing this ester, the olefin was formed, and was obtained instead of the ester. A mixture of 12.2 g of 4-isobutyl-2-methyl-4-nonadecanol, 11 g of 2-ethylhexanoic acid (boiling at 116-118° at 13 mm), and 1 ml of sulfuric acid was refluxed for seven hours. Vacuum fractionation of the reaction products yielded a fraction of b.p. 191-192° (4 mm); n_D^{20} 1.4526; d_4^{20} 0.8033; found MR 113.17; calculated MR 112.57.

Found %: C 85.26; H 14.79

$C_{24}H_{48}$. Calculated %: C 85.63, H 14.37

Hydrogenation of this olefin fraction was carried out over Raney nickel for nine hours at 130°, the initial pressure of hydrogen being 145 atm. The hydrogenation product boiled at 192-193° at 3 mm and froze to a crystalline substance at −16; it had n_D^{20} 1.4510; d_4^{20} 0.8013, found MR 113.76; calculated MR 113.03.

Found %: C 85.45; H 14.62

$C_{24}H_{50}$. Calculated %: C 85.12; H 14.88

5-Ethyl-2-methyl-4-(2-methylallyl)-1-nonen-4-ol. 2-Ethylhexanoic acid (b.p. 116-118° (13 mm); n_D^{20} 1.4259; d_4^{20} 0.9072) was converted into its methyl ester (b.p. 64-67° (14.5 mm); n_D^{20} 1.4142; d_4^{20} 0.8731). In accordance with Yarovsky's method, a mixture of 45 g of methyl 2-ethylhexanoate and 144 g of 2-methylallyl chloride dissolved in 300 ml of ether was added to 50 g of magnesium in 300 ml of ether. The mixture was heated for ten hours, and decomposition was then effected with water and ammonium chloride. An 80% yield of 5-ethyl-2-methyl-4-(2-methylallyl)-1-nonen-4-ol was obtained; b.p. 131-132° (10 mm); n_D^{20} 1.4660; d_4^{20} 0.8674, found MR 76.12; calculated MR 76.68.

Found %: C 80.36; H 12.41

$C_{16}H_{30}O$. Calculated %: C 80.60; H 12.68

The alcohol was hydrogenated under the same conditions as those used for the above-described diolefinic alcohol. The product was an alcohol of composition $C_{16}H_{34}O$, b.p. 124-125° (10 mm); n_D^{20} 1.4463; d_4^{20} 0.8386; found MR 77.61; calculated MR 77.14.

Found %: C 79.23, H 14.00

$C_{16}H_{34}O$. Calculated %: C 79.26; H 14.14

5-Ethyl-4-isobutyl-2-methylnonane. Dehydration of 10 g of the alcohol $C_{16}H_{34}O$ was effected by Landa's method [4], the alcohol being heated for three hours at 180° with 1.5 g of anhydrous zinc chloride. A mixture of olefins of composition $C_{16}H_{32}$ was obtained they had b.p. 120° (10 mm); n_D^{20} 1.4429; d_4^{20} 0.7853; found MR 75.70; calculated MR 75.62.

Hydrogenation under the conditions given above yielded a paraffin hydrocarbon boiling at 108-109° at 10 mm and freezing at −90°; it had n_D^{20} 1.4421; d_4^{20} 0.7836.

Found %: C 85.19; H 14.95

$C_{16}H_{34}$. Calculated %: C 84.85; H 15.14

SUMMARY

1. It has been shown that the reaction of methyl palmitate with 2-methylallylmagnesium chloride proceeds mainly according to the normal scheme, 2-methyl-4-(2-methylallyl)-1-nonadecen-4-ol being obtained in 56% yield. The yield of palmitone (16-hentriacontanone), formed by the anomalous reaction, was only 8%.

2. When the reaction was carried out with the methyl ester of an acid of lower molecular weight but of branched structure – 2-ethylhexanoic acid – the yield of the corresponding tertiary alcohol was as high as 80%, and no anomalous products were formed.

LITERATURE CITED

[1] A. D. Petrov, K. I. Karasev, and M. A Cheltsova, J. Gen. Chem., 6,522 (1936); A. D. Petrov and M. S. Malinovsky, J. Gen. Chem., 7, 565 (1937); A. D. Petrov and E. B. Sokolova, J. Gen. Chem., 8, 199 (1938); A. D. Petrov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1938, 347; A. D. Petrov and N. A. Roslova, J. Gen. Chem., 10, 937 (1940), A. D. Petrov, Bull. Acad. Sci., USSR, Div. Chem. Sci., 1950, 209.

[2] H. J. Shine, K. E. Turner, Nature 158, Aug. 3, 170 (1946).

[3] A. D. Petrov and E. A. Chernyshev, Prog. Chem., 22, 10 (1953).

[4] St. Landa, Collection 1 (1930), 520; 2 (1931), 367; 4 (1932), 538.

[5] Hickinbottom, Schluchtere, Nature, 19, 155 (1945).

Received December 15, 1954

N. D. Zelinsky Institute of Organic Chemistry of the
USSR Academy of Sciences

A. V. DUMANSKY, Corresponding Member of the Academy of Sciences of the USSR and Active Member of the Academy of Sciences of the Ukrainian SSR

Dear Anton Vladimirovich:

The Division of Chemical Sciences of the Academy of Sciences of the USSR and the Editorial Board of the Bulletin of the Academy of Sciences of the USSR, Division of Chemical Sciences, congratulate you on the attainment of the age of seventy-five years.

You have devoted the whole of your creative life to work on colloid chemistry, of which you are founder, propagandist, and successful exponent. You have created the Soviet school of colloid chemists. You are the originator and permanent editor of the Colloid Journal.

Your scientific, organizing, and teaching work has made a large and valuable contribution to the development of Soviet science.

We hope that there still lie before you many years of vigor, of health, and of fruitful labors devoted to the welfare of our beloved Fatherland.

Note: The photograph accompanying this salutation has not been reproduced in this translation because of the limitations of the printing process used. Publisher.

BLANK
PAGE

EXPERIMENTAL DETERMINATION OF THE SEQUENCE OF SUCCESSIVE ELEMENTARY REACTIONS OF ATOMS AND RADICALS

L. I. Avramenko and R. V. Kolesnikova

Detailed study of mechanisms of chemical reactions proceeding via intermediate stages in which radicals and atoms take part is important not only for the understanding of the actual process of chemical change, but also for the solution of practical problems. The existing concepts of the mechanism of chemical changes in which radicals take part, e.g. oxidative processes, are inadequate. Thus, various views have been expressed in the literature [1-9] on the processes of peroxide and aldehyde formation in the oxidation of hydrocarbons. Some authors consider that peroxides are primary oxidation products, and alcohols and aldehydes are secondary products; other authors consider that peroxides and aldehydes are formed simultaneously and independently.

In itself, therefore, the concept of a reaction proceeding via atom and radical formation is insufficient to enable the actual mechanism of a complex reaction to be understood and to be described quantitatively. It is necessary to have experimental proof of the existence of one or another kind of radicals in the reaction zone. Moreover, it is necessary to know what reactions can be given by the radicals and what the rate constants of these reactions are. However, many difficulties lie in the way of an extensive study of the elementary reactions of atoms and radicals. These difficulties arise from various causes, one of the most important being the shortness of the lives of atoms and radicals. This last circumstance makes it necessary to use special methods for the study of the reactions of atoms and radicals.

In our investigations of the elementary reactions of oxygen and hydrogen atoms, we have found a method that enables us to obtain information about the elementary reactions of the atoms from an examination of the ultimate reaction products. It is much easier to make measurements on the ultimate products, rather than the intermediates, but in order to obtain information about actual elementary reactions it is first necessary to know the order in which the reactions occur, since a given ultimate product can often be obtained either by a single elementary act, or by several successive elementary processes.

We propose a method that enables the sequence of the elementary reactions to be determined experimentally from the behavior of the ultimate reaction products. This method is illustrated by the reactions of atomic oxygen with various substances. The applicability of the method is not confined solely to the reactions of oxygen atoms, but may be extended to atoms and radicals of all kinds.

The apparatus in which the experiments were carried out is shown diagrammatically in Fig. 1. The whole of the apparatus was constructed of molybdenum glass. Atomic oxygen could be prepared in the apparatus either from water vapor or from molecular oxygen, a stream of the substance being passed through the discharge tube 2, a conical nozzle 1 (length 30 mm; diameter 1.5 mm at the discharge-tube end and 5 mm at the reaction-vessel end), and the reaction vessel 3. For a linear streaming velocity of 300-800 cm per second this method of construction enabled fuel to be passed into the reaction vessel over a wide range of concentrations without the slightest signs of diffusion of fuel into the discharge. Any such diffusion was readily detected visually by change in the color of the discharge at the nozzle. Fuel was supplied through the capillary 4, which was fused into the reaction vessel 3. The fuel supply was regulated by the valve 5, which was found to be very convenient for the regulation of a gas stream, being equivalent to a whole range of capillaries varying in diameter. The combustible gases were kept in a gas holder, and were passed into the calibrated flask 14 before the experiment. The consumption of gas was measured with the aid of the flask 14 and the manometer 15. Reaction products that could be condensed with liquid air were collected in the detachable trap 10. Carbon monoxide was determined by oxidation over Hopcalite in the tube 12, through which the stream passed after leaving the trap 10; CO_2 was then frozen out in the trap 18. The interchangeable joints 6, 7, 8, and 9 were used for the introduction of oxygen (or any other gas required) into various parts of the reaction zone. The vessel 11 served for the taking and separation of samples of gaseous products; they were taken from the trap 10 and collected by a freezing-out process.

It should be noted that in such an apparatus, atomic oxygen may be prepared from water vapor without any appreciable admixture of molecular oxygen [10]. That this is so follows from the fact that the addition of oxygen molecules in the reaction zone results in the appearance of new products or in increase in the amount of the products formed when no addition of oxygen is made. This indicates that radicals are present in the reaction zone which yield these products by reaction with molecular oxygen. The utilization of this fact is of great importance in our method for determining the order in which elementary reactions occur.

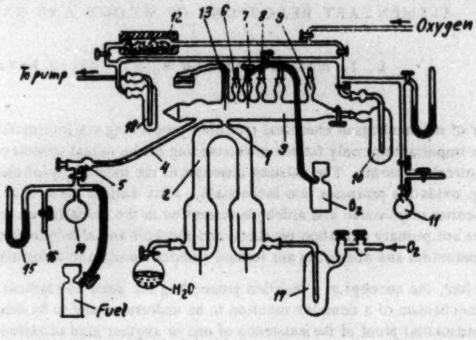


Fig. 1. Diagram of apparatus: 1-conical nozzle; 2-discharge tube; 3- reaction vessel; 4-capillary; 5-valve; 6, 7, 8, and 9-interchangeable joints, through which additions are made; 10- detachable trap; 11-transfer vessel; 12-tube containing Hopcalite; 13 - thermocouple; 14- calibrated flask; 15-manometer; 16- side tube required when liquid fuels are used; 17 - trap for drying gas (O_2 or H_2); 18- detachable trap

In order to avoid confusion in terminology it is necessary to give some definitions. A primary reaction is a reaction of an original active center (oxygen atom) with an original fuel molecule, or the reaction of an original radical with an oxygen molecule. Quadratic reactions are reactions between primary products (molecules and radicals) and the original active center (oxygen atom). Cubic reactions are reactions between quadratic reaction products (molecules and radicals) and the original active center. Secondary reactions are reactions between primary (not to be confused with "original") radicals obtained in primary reactions and molecular compounds having no free valencies, and also the decomposition reactions of primary radicals and molecules.

Hence, primary and secondary products are formed by a single act of interaction with the original active center, whereas quadratic reactions require two acts, and cubic three acts, of interaction with the original active center.

Concentrations will be represented as follows: original substance A, oxygen atoms O, primary product B, quadratic product D, cubic product F, secondary product C, and various radicals R. The corresponding reaction constants will be denoted by K with various subscripts and superscripts. The general scheme can be represented as follows:

$$O + A \xrightarrow{K_1} \begin{cases} B & K_1'' \\ B_1 + R & K_1' \end{cases} \qquad \text{primary}$$

$$R + O_2 \xrightarrow{K_2} C + R_1 \qquad K_2' \qquad \text{secondary}$$

$$O + B \text{ (or } C) \xrightarrow{K_4} \begin{cases} D & K_4' \\ D_1 + R_2 & K_4'' \end{cases} \qquad \text{quadratic}$$

$$O + D \xrightarrow{K_3} \begin{cases} F & K_3'' \\ F_1 + R_3 & K_3'' \end{cases} \qquad \text{cubic}$$

$$O + O + M \xrightarrow{K'M} O_2 + M$$

$$O + \text{wall} \xrightarrow{K_3}$$

On the basis of this general scheme the following kinetic equations can be written for A, B, C, D, E, and O:

$$\frac{dA}{dt} = -K_1(A)(O)$$

$$\frac{dB}{dt} = K_1^1(A)(O) - K_4(B)(O)$$

$$\frac{dC}{dt} = K_2^1(R)(O_2) - K_4(C)(O)$$

$$\frac{dD}{dt} = K_4^1(B)(O) - K_3(D)(O)$$

$$\frac{dF}{dt} = K_3^1(D)(O)$$

$$-\frac{d(O)}{dt} = K_1(O)(A) + K_4(O)(B) + K_3(O)(D) + K_M(O)^2 + K_0(O)$$

By the simultaneous solution of these equations with application of the limiting conditions [when $A = A_0$, $(O) = (O)_0$ and $B = D = C = F = 0$;] and when $A = A_f$, $B = B_f$, $D = D_f$, $F = F_f$, $C = C_f$, and $(O)_f = 0$ we obtain expressions for the quantities of interest to us, B, C, D, F, and O, as functions of A.

For the primary product B reacting with atomic oxygen an expression of the following form is obtained:

$$B_f = \frac{K_1^1}{K_1 - K_4} A_0 \left(a^{\frac{K_4}{K_1}} - a\right). \tag{1}$$

in which B_f denotes the final concentration of the primary product (the concentration at the end of the reaction zone), A_0 denotes the initial concentration of the original substance, and a denotes the ratio A_f/A_0. For the secondary product C an expression similar to (1) is obtained:

$$C_f = \frac{K_1^1 K_2^1}{K_2(K_1 - K_4)} A_0 \left(a^{\frac{K_4}{K_1}} - a\right). \tag{2}$$

in which C_f is the final concentration of the secondary product.

For the quadratic product D an expression of the following form is obtained:

$$D_f = \frac{K_4^1 K_1^1}{K_1 - K_4} A_0 \left[\left(\frac{1}{K_4 - K_3} - \frac{1}{K_1 - K_3}\right) a^{\frac{K_3}{K_1}} - \frac{1}{K_4 - K_3} a^{\frac{K_4}{K_1}} + \frac{a}{K_1 - K_3}\right], \tag{3}$$

in which D_f is the final concentration of the quadratic product.

For the cubic product F, which does not react further with atomic oxygen, an expression of the following form is obtained:

$$F_f = \frac{K_4^1 K_1^1}{K_4 - K_1} A_0 \left[\left(\frac{1}{K_4 - K_3} - \frac{1}{K_1 - K_3}\right)\left(a^{\frac{K_3}{K_1}} - 1\right) - \frac{K_3}{K_4(K_4 - K_3)}\left(a^{\frac{K_4}{K_1}} - 1\right) + \frac{K_3}{K_1(K_1 - K_3)}(a - 1)\right], \tag{4}$$

in which F_f is the final concentration of the cubic product.

The relation between a and A is given by the formula:

$$A_0 = \frac{-\frac{K_0}{K_M} + \left[(O)_0 + \frac{K_0}{K_M}\right] a^{\frac{K_M}{K_1}}}{(a + b + c)a^{\frac{K_M}{K_1}} - \mathrm{a}a^{\frac{K_4}{K_1}} - \mathrm{b}a^{\frac{K_4}{K_1}} - \mathrm{c}a} \tag{5}$$

in which $(O)_0$ is the initial concentration of atomic oxygen;

$$\mathrm{a} = \frac{K_1}{K_1 - K_M} + \frac{K_1 K_4}{(K_4 - K_1)(K_1 - K_M)} - \frac{K_1 K_3 K_4}{(K_4 - K_1)(K_1 - K_3)(K_1 - K_M)};$$

$$b = \frac{K_1K_3K_4}{(K_4 - K_1)(K_4 - K_3)(K_4 - K_M)} - \frac{K_1K_4}{(K_4 - K_1)(K_4 - K_M)};$$

$$c = \frac{K_1K_3K_4}{(K_4 - K_1)(K_1 - K_3)(K_3 - K_M)} - \frac{K_1K_3K_4}{(K_4 - K_1)(K_4 - K_3)(K_3 - K_M)};$$

The physical significance of *a* is such that it can vary from zero to unity. When the constants K_1, K_3, K_4, K_M, and K_0 are given definite values, values of A_0 can be found for various values of *a*.

As an example we will make calculations for ratios of constants that are probable for the reaction of oxygen atoms with the ethane molecule, namely:

$$\frac{K_4}{K_1} = 10; \quad \frac{K_3}{K_1} = 0.5; \quad \frac{K_M}{K_1} = 0.05; \quad \frac{K_0}{K_M} = 6.5 \cdot 10^{15}; \quad (O)_0 = 8 \cdot 10^{14}.$$

The constants K_M and K_0 are known [10]. We then obtain: $a = 1$, $b = -0.105$ and $c = 2.34$. Substituting all the numerical values of constants in Equation 5, we obtain:

$$A_0 = \frac{6.5 \cdot 10^{15} - 7.3 \cdot 10^{15} a^{0.05}}{a - 0.105 a^{10} - 3.235 a^{0.05} + 2.34 a^{0.5}} \qquad (6)$$

Fig. 2 represents the relation between a and A_0 according to Equation 6. For other ratios of the constants K_1, K_4, and K_3, the curves obtained are similar in form to that in Fig. 2.

By a suitable choice of constants the relation between *a* and A_0 can be determined for the reaction of oxygen atoms with any other molecule. By the use of the known dependence of *a* on A_0, the relation of B_f, D_f, and F_f to A_0 can be represented graphically.

Fig. 3 gives the curves for the dependence of B_f, D_f, and F_f on A_0. These curves have been constructed with the aid of Equations 1, 3, and 4 and the calculated relation of *a* to A_0 for ethane, and it was assumed the $K_4^1 = K_4$ and $K_1^1 = K_1$. The equality of these constants occurs when the original substance forms only one primary product, which then forms only one quadratic product.

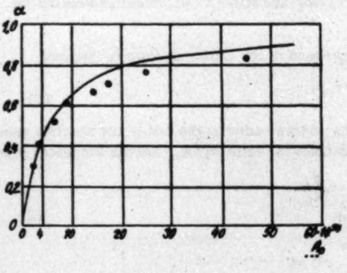


Fig. 2. Curve for the dependence of a on A_0 (the continuous line represents the calculated relation for ethane, and the points represent the experimental values for ethane)

In Fig. 3 the differences between the primary, quadratic, and cubic reaction products are clearly seen; the curve for the cubic product bends over toward the maximum value at a lower value of A_0 than the curve for the quadratic product, which itself bends over at a lower value of A_0 than the curve for the primary product. Also, the curves for the cubic and quadratic products have maxima but the curve for the primary product has only a limiting value; the value of the maximum on the curve for the quadratic products is less than half of that of the limiting value for the primary product.

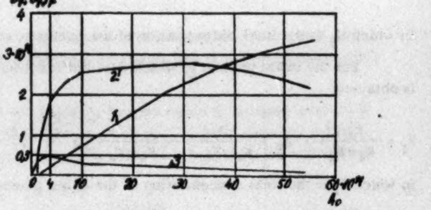


Fig. 3. Curves for the dependence on A_0 of the final concentrations of the primary, quadratic, and cubic products of the reaction of oxygen atoms with ethane (the calculated value for a for ethane is used): 1 - primary product B_f; 2 - quadratic product D_f; 3- cubic product F_f

This picture is readily understood when physical aspects of the phenomena occurring under the conditions of the experiment are examined. When the concentration of the original substance is low, atomic oxygen may react not only with this substance, but also with primary and quadratic reaction products. As the concentration of the original substance is increased at a constant concentration of atomic oxygen, an increasing proportion of the oxygen atoms will react only with the original substance and a diminishing proportion will react with reaction products. Finally, at sufficiently high concentrations of the original substance, oxygen atoms will react only with this substance and only the primary product will be formed. Further increase in A_0 will no longer result in a rise in the final concentration of the primary product, since all of the oxygen atoms produced will participate only in the

primary reaction. Hence, at very high fuel concentrations, the amount of oxygen-containing primary product formed will attain its limiting value. This limiting value should be equivalent to the amount of atomic oxygen passed into the vessel during the same period of time.

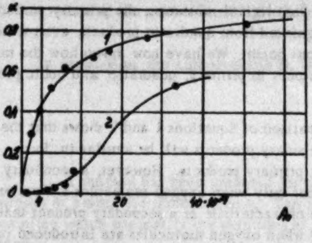


Fig. 4. Experimental curves for the dependence of a on A_0: 1- for ethane; 2- for formaldehyde

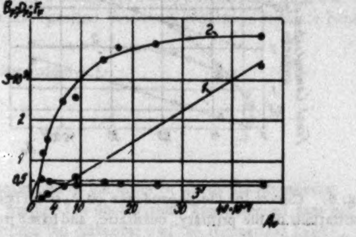


Fig. 5. Curves for the dependence on A_0 of the final concentrations of the primary, quadratic, and cubic products of the reaction of oxygen atoms with ethane (the experimentally found value of a for ethane is used): 1- primary product; 2- quadratic product; 3- cubic product

It will be evident that the amount of quadratic product at its maximum cannot be more than half the amount of primary product at its limiting value, and the amount of cubic product cannot attain more than one-third of the limiting value for the primary product, for the quadratic product requires two oxygen atoms for its formation, and the cubic product requires three.

The value of a and its relation to A_0 can be measured experimentally under the conditions we have employed. These measurements were carried out for a few substances. The results of such measurements with ethane as an example of fuels that do not react readily (Curve 1) and formaldehyde as an example of fuels that react readily (Curve 2) are represented graphically in Fig. 4.

Comparison of Figures 2 and 4 shows that curves for the dependence of a on A_0 obtained by experiment and by calculation are very close together. The points lying along the calculated curve in Fig. 2 represent the experimental results. The satisfactory accord between experimental and calculated curves indicates that the ratios of the reaction-rate constants K_1, K_3, and K_4 that we have assumed for ethane in the calculations are close to their true values.

Fig. 5 shows curves for the dependence on A_0 of the final concentrations of the primary, quadratic, and cubic products of the reaction of oxygen atoms with ethane. These curves are constructed from Equations 1, 3, and 4, the values taken for a being those obtained experimentally. In the construction of the curves it was assumed that $K_1^1 = K_1$ and $K_4^1 = K_4$. Fig. 5 shows the difference between the primary products and the quadratic and cubic products.

A mathematical and graphical analysis that we have carried out for the functions B_f, D_f, and F_f shows that, whatever ratios of K_1, K_4, and K_3 may be assumed, the conclusions concerning the different forms of the functions B_f, D_f, and F_f always hold good. When any particular reaction product is formed not only by a purely primary reaction, nor only by a purely quadratic reaction, but by both primary and quadratic reactions, i.e. by a mixed method, a more complex picture is obtained. The complexity, however, does prevent us from explaining the essence of the phenomenon.

For a mixed product the following expression was obtained;

$$\Sigma_f = \frac{K_1^1}{K_1 - K_4} \cdot A_0 \left({}^{\frac{K_4}{K_1}} - a + \frac{K_4^1}{K_4 - K_3}\, a^{\frac{K_3}{K_1}} - \frac{K_4^1}{K_1 - K_3}\, a^{\frac{K_3}{K_1}} - \frac{K_4^1}{K_4 - K_3}\, a^{\frac{K_4}{K_1}} + \frac{K_4^1}{K_1 - K_3}\, a \right). \quad (7)$$

in which Σ_f is the final concentration of the mixed product.

By the use of the known relation of a to A_0, calculated from Equation 6 or determined experimentally, graphs may be constructed for the purely primary, purely quadratic, and mixed reaction products. These are given in Fig. 6 for the reaction of ethane with atomic oxygen, the experimentally found values of a being used. Fig. 6 shows the difference between the curve for the mixed product and those for the purely primary and purely quadratic products: the curve for the mixed product, like that for the quadratic product, bends over at a lower value of A_0 than the curve for the primary product, but with increase in A_0 the curve for the mixed product does not attain a maximum, as the curve for the quadratic product does, but continues to rise linearly, like the curve for the primary product. When the linear part of the curve for the mixed product (Fig. 6, Curve 3) is produced to meet the axis of ordinates (broken line),

the intercept formed corresponds to the value of the maximum final concentration of the quadratic product.

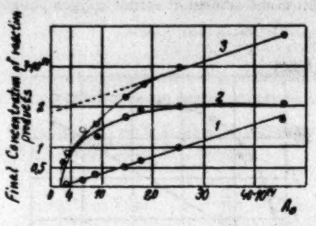


Fig. 6. Curves for the dependence on A_0 of the final concentrations of the primary, quadratic, and mixed products of the reaction of oxygen atoms with ethane (the experimentally found value of a for ethane is used): 1- purely primary product; 2- purely quadratic product; 3 - mixed product

In this way, from the form of the curves for the final concentrations (and therefore also for the rates of formation of various reaction products) as functions of the initial concentration of the original substance, the primary products can be distinguished from quadratic products, even when mixed reactions occur. We have now shown how the matter stands with respect to primary, quadratic, and cubic products.

A comparison of Equations 1 and 2 shows that the curves for secondary products will be similar in form the curves for primary products. However, a secondary product can appear only when oxygen molecules are present. It is therefore characteristic of a secondary product that it will appear when oxygen molecules are introduced into the reaction zone, so long as its curve is similar in form to that of the primary product.

In order to verify the correctness of the theoretical conclusions, we shall make use of experimental results already published.

Fig. 7 shows graphs for the dependence of the rates of formation (the product of the final concentration, the rate of flow, and the cross-sectional area of the vessel) of ethanol, formaldehyde, CO, and CO_2 on the product of the rate of flow and the concentration of the original ethane. These graphs were constructed from the data in Table 2 of our previous communication [11]. It will be seen that the curves for alcohol and formaldehyde are greatly different in form from those of CO and CO_2. A comparison of the experimental curves (Fig. 7) with the theoretically calculated curves (Figures 3 and 5) indicates that the curves for CO and CO_2 have the form typical for quadratic and cubic products, whereas the curves for alcohol and formaldehyde are typical for primary products.

Actually, it can scarcely be doubted that products such as CO and CO_2 are not formed in the reaction of ethane with oxygen atoms as the result of the primary collision of an oxygen atom with a fuel molecule. However feasible schemes for the formation of these products may be from the point of view of energy changes, it must always be true that for the formation of CO and CO_2 reactions must occur in which at least two atoms of oxygen enter successively into the reaction.

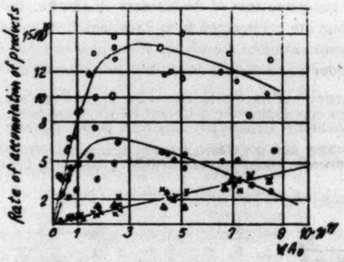


Fig. 7. Curves for the dependence of rates of formation of products of the reaction of atomic oxygen with ethane on the product of the rate of flow and the concentration of original ethane: ▲ – ethanol; x – formaldehyde; o – CO; ● – CO_2

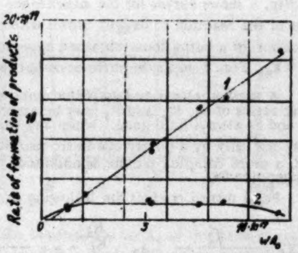


Fig. 8. Curves for the dependence of the rate of formation of reaction products on the product of the rate of flow and the initial concentration of the original formaldehyde: 1- CO; 2. CO_2

Fig. 8 shows curves for the rates of formation of CO and CO_2. It is constructed from data obtained in an investigation of the reaction of atomic oxygen with formaldehyde [12]. In Fig. 8 the difference in the variation of the yields of the primary product CO and the secondary product CO_2 is clearly visible.

The bend in the curve for the quadratic product begins at much lower values of wA_0 than that in the curve for the primary CO. The results of investigations of reactions of atomic oxygen with acetaldehyde [12] and with methane [13] also provide excellent illustrations of the correctness of the method, but the significance of these results is not confined only to the illustration of the method, for they are of great importance in the study of the mechanism of the formation of oxygen-containing substances by the reactions of oxygen atoms. Moreover, this sequence-determining method enables us to determine the rate constants of the elementary reactions of the original atoms and radicals, and it also enables us to determine the initial concentrations of the original atoms and radicals from the limiting values of the concentrations of the primary products. This last question, however, requires a separate examination.

In conclusion, the authors thank D. G. Knorre for valuable discussions.

SUMMARY

1. A method has been proposed for the experimental determination of the order in which the elementary reactions of atoms and radicals occur. The theoretical basis of the method has been given. Experimental data has been cited which exemplify the reactions of atomic oxygen and confirm the correctness of the theoretical background.

2. It has been shown that the method enables reaction products formed by a primary elementary act of an atom or radical to be distinguished from those arising by secondary and subsequent acts.

3. On the basis of the results obtained by this method, i.e. on the basis of regularities observed in the concentrations of the final products, conclusions may be drawn concerning the actual elementary reactions of atoms and radicals that are occurring.

LITERATURE CITED

[1] Problems of Kinetics and Catalysis, Collection 4, State Chem. Press, Leningrad, 1940 (see paper by A. N. Bakh, S. S. Medvedev, K. I. Ivanov, and M. B. Neiman).

[2] K. I. Ivanov, Intermediate Products and Intermediate Reactions in the Autoxidation of Hydrocarbons, State Fuel Tech. Press, 1949.

[3] W. Bone, J. Chem. Sci. 83, 1074 (1903); Proc. Roy. Soc. A129, 434 (1930); A137,243 (1932); A143, 16 (1933); A154, 297 (1936).

[4] A. Egerton, F. Smith and A. Ubbelohde, Phil. Trans. 234, 433 (1935); A. S. Sokolik, Technology in the Air Force 4, 77 (1936).

[5] D. M. Newitt, Proc. Roy Soc. A140, 426 (1933); A147, 555 (1934); A154, 329 (1936); J. Chem. Soc. 1937, 165, 61669.

[6] R. A. Day, R. N. Pease, J. Am. Chem. Soc. 51, 1839 (1929); 57, 9296 (1935).

[7] A. R. Ubbelohde, Proc. Roy. Soc. A152, 354 (1935).

[8] M. B. Neiman, A. A. Dobrinskaya, and V. I. Gnyubkin, Mechanism of the formation of the butane cool flame, Moscow, 1940.

[9] N. N. Semenov, Prog. Chem. 20, 673 (1951).

[10] L. I. Avramenko, J. Phys. Chem. 23, 790 (1949).

[11] L. I. Avramenko and R. V. Kolesnikova, Proc. Acad. Sci. USSR 89, 1037 (1953).

[12] L. I. Avramenko and R. V. Lorentso, J. Phys. Chem. 26, 1084 (1952).

[13] L. I. Avramenko and R. V. Kolesnikova, Proc. Acad. Sci. USSR 91, 107 (1953).

Received June 18, 1954

Institute of Chemical Physics of the
USSR Academy of Sciences

BLANK
PAGE

STRUCTURE OF SODIUM BOROSILICATE GLASSES IN ITS RELATION TO THE PHENOMENON OF OPALESCENCE

COMMUNICATION 3. COMPARISON OF THE RESULTS OF INVESTIGATIONS ON SODIUM BOROSILICATE GLASSES AND ON POROUS PRODUCTS OBTAINED FROM THEM BY LEACHING

E. A. Porai-Koshits, S. P. Zhdanov, and D. I. Levin

1. Relation between the Structures of the Original and the Porous Glasses

In previous communications [1, 2] we have made a survey of existing views on the causes of the opalescence of certain sodium borosilicate glasses and have described the results of experimental investigations on the Rayleigh scattering of light by the original glasses and on the structure of porous glasses prepared from them by the action of acids. In the light of these results the phenomenon of opalescence must be given a different interpretation from that advanced in the literature.

Experimental results given in the second communication have established that there is a close relationship between the structures of the original and porous glasses. It was in fact established, as a result of investigation of the structure of porous glasses by three independent methods (adsorption, low-angle scattering of X-rays, and examination under the electron microscope), that these glasses have a binary disperse structure. It was found that porous glasses have a silica skeleton having large cells or channels, the diameter of which, depending on the composition of the original glass, varies from tens to thousands of angstrom units. Within the channels there is a secondary fine structure formed from highly dispersed silicic acid, and the pores of this structure are not more than a few tens of angstrom units in diameter. The extent to which the main channels of the silica skeleton are packed with hightly dispersed silicic acid depends on the heat treatment given to the original glass and on its composition; it may vary greatly. When they are filled compactly, the intensity of the low-angle scattering of X-rays falls to an insignificant value as a result of the small difference in electron density between the channel walls and the substance filling the channels; the sorption method, however, reveals the presence of extremely fine pores having radii of the order of 10 A. When there is an almost complete absence of silicic acid in the channels, low-angle scattering gives a diffraction picture on the X-ray film in a very short time, and the large pores can be detected by the sorption method even when the porous glasses have not been treated with alkali.

When these results were considered in relation to the opalescence of the original glasses it became quite clear that opalescence is completely independent of the secondary structure, since porous glasses that are identical with respect to the dispersity of secondary silicic acid can be obtained both from strongly opalescent glasses and from completely transparent glasses. It was found also that there is an extremely close relationship between opalescence and the structure of the silica skeleton, the channels of which vary in diameter from almost 1000 A to 80-160 A, according as the original glass is opalescent or clear.

On the basis of these facts it is quite logical to suppose that the silica skeleton is present in sodium borosilicate glassss right from the beginning already before leaching. The strong scattering of light by the original glasses their opalescence is then readily explained by the differentiation of sodium borosilicate glasses, according to composition, into silica and borate components, this differentiation being the basis of the possibility of the preparation of a porous product by leaching. From this point of view, the variation in the intensity of light scattering is associated with variation in the degree of dispersion of the second component (which is dispersed within the skeleton), and hence with variation in the dimensions of the channels and walls of the silica skeleton.

The correctness of this interpretation of the phenomenon of opalescence is confirmed also by the rather high temperature at the lower limit of the opalescence zone, by the rapid increase in opalescence with further rise in temperature*, and by the dependence of the level of the higher limit of the zone on the composition of the glass. Actually, if the increase in the intensity of light scattering is associated with enlargement of the channels of the silica skeleton, the temperature at which opalescence begins and the rate at which opalescence increases in intensity should depend on the viscosity of the glass, which falls appreciably in the temperature range of 550-700°, approximately. Comparisons of opalescence in glasses varying in composition show that the upper temperature boundary of the opalescence zone becomes lower as the amount of silica in the glass is reduced: the glass Na 75-20 (75% SiO_2) becomes clear when heated to 710-715°, whereas the glass Na 60-30 (60% SiO_2) becomes clear at 685-690°*.

---

* See Communication 1, Figures 1 and 4 [1].

It must be mentioned that there is another, widely held view on the causes of opalescence. This view is in conflict with that discussed above, for it envisages a complete rearrangement of molecular bonds during leaching, and a further rearrangement during the alkali treatment of the resulting porous glass, i.e. it rejects the possibility of the existence of any sort of relationship in structure between the original glass and the porous glass, before and after alkali treatment. It is desirable, therefore, to refer to other experimental facts that confirm the existence of this relationship and show that the dimensions of the pores of the leached products can be regarded as identical with those of the regions of heterogeneity in the original glasses.

1. That the original and the porous glasses have a common structure is confirmed by the close dependence of the volume of pores and the pore dimensions on the composition of the original glass and the thermal treatment to which it has been submitted [1, 2]. Sorption and X-ray investigations have shown that in porous glasses both the total volume of pores and the pore radii increase with increase in the amount of the component of the original glasses that passes into solution (B_2O_3 and Na_2O). Also, a characteristic of porous glasses distinguishing them from silica gels is the small total volume of pores. These structural peculiarities of porous glasses indicate that, unlike silica gels, they are not completely new formations, their structures being largely predetermined by the structures of the original glasses. This conclusion is valid for all porous glasses prepared from glasses containing not less than 60% of SiO_2 (they include also glasses capable of becoming opalescent). Glasses that are poor in silica (containing less then 35% of SiO_2) yield spongy gel-like products, in no way different in structure from the usual silica gels. These products consist entirely of secondary structure, but they can no longer be regarded as porous glasses.

2. We have recently repeated an experiment originally suggested by S. E. Krasikov, and first performed by him; we modified the conditions somewhat. A fine filament of the original glass Na 70-23, diameter about 0.7 mm, was placed freely on two supports separated by a distance of 120 mm. A rod was positioned in the center of the filament so as to depress it by 5.74 mm, the depression being measured with an MIR-1 measuring microscope, suitably adapted for the purpose. In this form the filament was placed in a bath and leached with 3 N HCl for 32 hours at room temperature. When the load was removed (removal of the rod), the filament, now thoroughly treated throughout its cross section, rapidly straightened itself, so that already after the first minute the depression had diminished to 1.12 mm, after the second to 1.10 mm, after the twentieth to 0.95 mm, and so on. After 2 hours 30 minutes the depression was 0.72 mm, and after 38 hours it had reached 0.36 mm, i.e. about 6% of its maximum value, and even then slow straightening of the filament was continuing. This experiment was varied in various ways, but in all cases it was confirmed that the structure of the original glass is largely retained in the porous glass, for the leaching process did not remove internal strains produced by the applied load.

3. Already in 1942 one of the authors of this paper carried out an X-ray investigation of a sodium borosilicate glass that was capable of becoming opalescent [3]. In 1953 these experiments were continued under improved experimental conditions and with a large assortment of glasses (including Na 70-23 and Na 75-20) [4].

The X-ray phorographs were taken in vacuum cameras with the aid of MoK_{α} radiation rendered monochromatic by reflection at a calcite monocrystal. The phorographs were exam-

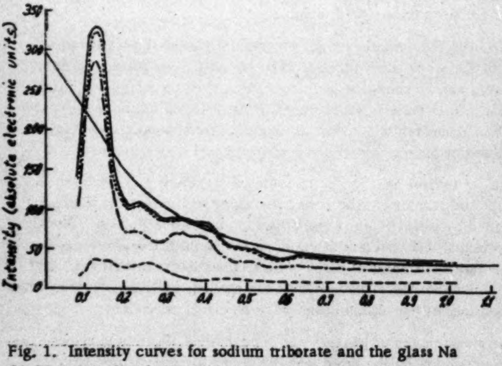


Fig. 1. Intensity curves for sodium triborate and the glass Na 70-23 (original and porous): ——— Na 70-23 (experimental); —·—·— porous glass; . . . . sum (I' - ($Na_2O \cdot 3B_2O_3$ + porous glass); - - - - - - - - $Na_2O \cdot 3B_2O_3$.

---

* See Communication 2, Fig. 10 [2].

ined with a recording microphotometer and intensity curves were determined, the intensity being expressed in absolute electronic units (polarization, absorption, and incongruent scattering were taken into account). It was again confirmed that the intensity curve of the original glass can be represented as the sum of the curves for vitreous sodium borate and for the porous glass obtained by treating the original glass with hydrochloric acid (Fig. 1). This provides direct proof that silica skeleton, regarded not only submicroscopically, but also at the atomic level, is already present in the original sodium borosilicate glasses and is not formed in the course of chemical reaction between the sodium silicates of borates of the original glass and the acids with which it is treated. The absence of even a small discrepancy between the summative and experimental curves for the original glasses in the region of the main intensity maximum indicates how negligible is the effect of the boundary layer or of the intermediate layer, heterogeneous in composition, between regions differing in chemical composition and large in size in comparison with the transitional layer.

4. The common structure of the original and porous glasses is confirmed also by the striking symbatic relationship between the curves (which have obvious anomalies) for the dependence of many physical and chemical properties of the original glasses (density, refractive index, chemical stability, etc.) on temperature and the curves characterizing the structure of porous glasses prepared from the original glasses at the corresponding temperatures [5].

The dimensions of the regions consisting of dispersed component – evaluated from measurements of the diameters of the main channels of the porous products obtained by leaching – are 600-1000 A for opalescent glasses; they can be regarded as small in comparison with the wavelength of visible light, and light scattered by such regions should be mainly polarized, which is in accord with depolarization measurements in the opalescence zone [6].

When the temperature is raised above a value that is characteristic for each composition, the opalescence disappears as a result of a great reduction in the dimensions of the channels of the silica skeleton and a corresponding increase in the degree of dispersion of the second component, which has an extremely low viscosity at this temperature. The disappearance of opalescence is a phenomenon similar to that observed in liquid mixtures near to the temperature of complete solution. However, the glass does not become completely homogeneous, and at temperatures 50-100° above that at which opalescence disappears it continues to retain the two independent structures, the degree of dispersion, however, being much higher than it is in opalescent glasses. The dimensions of the regions of heterogeneity are now 80-150 A, again estimated from measurements of the diameters of the channels in porous glasses, and the distribution of the regions according to size is much narrower in clear glasses than in opalescent glasses.

With regard to the chemical composition of the component dispersed within the silica skeleton, the suggestion of Grebenshchikov [7] that sodium oxide undergoes redistribution between B_2O_3 and SiO_2 as the temperature changes – which he based on the analysis of the dry residue from the acid extract – has been confirmed in the present work. The formation of various compounds between Na_2O, B_2O_3, and SiO_2 within this component of the original glass will, in fact, result in a variation in the compactness with which the channels of the porous glass are filled with secondary silicic acid – and this is what is actually observed. Accepting Grebenshchikov's suggestions, we may describe the variation of the composition of the dispersed component with temperature as follows.

As low temperatures, when the change in the intensity of Rayleigh scattering is reversible and the main channels of the porous glass obtained by leaching are filled with not very closely packed secondary silicic acid, it is probable that reversible chemical reactions of some sort occur in the glass with the participation of all of the three oxides Na_2O, B_2O_3, and SiO_2. At the temperature of minimum scattering, which is characterized also by almost complete absence of secondary silicic acid in the main channels of the porous glass obtained by leaching, it must be assumed the $\mathrm{Na-O-B}\langle$ linkages are formed preferentially, rather than $\mathrm{Na-O-\overset{|}{\underset{|}{Si}}-}$linkages, which should facilitate dissolution of the dispersed component in the skeleton and the formation of clean channels. Finally, at temperatures in the opalescence zone, which is characterized not only by maximum scattering intensity, but also by the formation of a porous glass having channels that have an extremely compact filling of secondary silicic acid, it is most probable that sodium silicates take an active part in chemical leaching reactions, and these silicates, being hydrolyzed in the course of the leaching, are a source of silicic acid gel, which forms a compact filling in the channels (secondary structure).

When the temperature is raised above 550°, there is a rapid increase in the dimensions of the regions of heterogeneity which is accompanied by the appearance of opalescence, and this process, as pointed out in our first communication, is irreversible: if we begin to lower the temperature from some value in the opalescence zone, then a part of the curve from 530° to 20° can be reproduced (with a characteristic minimum at 530°), only at a high value of absolute intensity (curve a', b', c', Fig. 2). The reversibility of relative changes in this temperature region must be associated with the same processes of chemical redistribution, but they now occur in large regions of heterogeneity. Only when we pass beyond the temperature at which opalescence disappears do these large regions break down again into small ones, so that the whole process can be repeated once more.

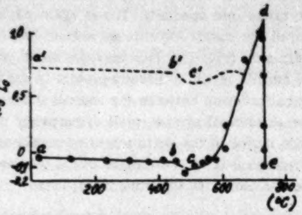


Fig. 2. Dependence of the intensity of light scattering on temperature for the glass Na 70-23

2. Microheterogeneous Structure of Complex Glasses

The facts discussed in the first section, and also the experimental results given in previous communications, confirm the general views of Grebenshchikov on the peculiar "submicroheterogeneity" of complex glasses, and they permit us to describe the structure of the sodium borosilicate glasses that we have studied in the following manner.

Sodium borosilicate glasses, that are capable of showing opalescence have a silica skeleton, and the cells of this skeleton are filled with a second component containing boron, sodium, and silicon oxides, which, according to the composition and temperature, form various chemical compounds. These regions of qualitative heterogeneity provide the source of the scattering of light in varying degree right up to strong opalescence. The peculiar "microheterogeneity" or "two-phase character" (the term " phase" is not, of course, to be understood in the sense of the classical definition) of sodium borosilicate glasses is not exceptional among complex glasses. It would be more true to say that these glasses form a more suitable object for investigation in the study of the general laws governing the structure of complex glasses, since they enable an approach to be made by a combination of different methods of X-ray structural analysis (scattering at high and at low angles) with other physicochemical methods. Similar properties are possessed by other alkali borosilicate glasses, such as potassium and lithium, and probably also by some phosphate and aluminosilicate glasses, etc.

In a recently published paper [8] describing an electron-microscope investigation of the vitreous silica in two commercial glasses of fairly complex composition, a lead glass, and some sodium borosilicate glasses having Na_2O contents of 16-50 mole-%, photographs are given that reveal the presence of a grain structure in all of the glasses, and the dimensions of the grains, depending on the composition and the thermal treatment of the glass, vary from 15-20 to 200 A. In some of the glasses the regions of heterogeneity are extremely regular in form. When the glass is drawn into filaments, the grains are drawn out into chains, which are oriented along the axis of the filament. A photograph of the silica skeleton obtained at the surface of one of the glasses as a result of its treatment with acid is of great interest. The authors consider that the glasses have heterogeneous structures and contain micellar regions that are higher in electron density and more regular in structure than the surrounding medium.

In a recently published paper, Indenbom [9] states that two different strain-relaxation zones occur in the glasses that he has investigated (their compositions are not given in the paper), these zones being associated with the occurrence of strains of the second kind that are compensated in micro-spaces. These strains result in anomalous birefringence, which does not disappear in the usual annealing process. The author associates these phenomena with the presence of two phases differing in softening temperature, i.e. with a microheterogeneous structure. The results of Debye and Bueche [10] on the intensity of light scattered at various angles from two optical glasses are to be interpreted in the same way. Using the theory proposed by Debye, the authors calculated the dimensions of the regions of heterogeneity from the scattering indicatrices; for the radii of the regions they found 296 A for borosilicate glass and 269 A for heavy flint glass. If we take the difference in the compositions of the glasses into account, these results are in close accord with the results of the investigation described in our second communication [2].

Already in 1943 [11] one of the authors of the present paper showed by X-ray investigation that certain binary glasses (sodium silicate, borosilicate, and sodium borate glasses) have "microheterogeneous" structures. Supplementary experiments carried out recently [4] have shown that for sodium silicate glasses a small amount of additional scattering of X-rays can be detected (not accounted for by the scattering of the components). This results from the presence of an intermediate "chemically disorganized" part of the glass, which binds the vitreous silica and sodium metasilicate together. This result indicates that the chemically homogeneous regions cannot be as large as those in sodium borosilicate glasses that are capable of becoming opalescent. The additional scattering found at relatively low angles $\left(\frac{\sin\theta}{\lambda} \approx 0.15\right)$, must be associated with the effect of matter distributed at the surface of each chemically homogeneous region or "phase", and the significance of such a boundary effect will grow as the size of such a region is reduced. It may be mentioned that a similar result was recently obtained by Danilov [12], who made an X-ray investigation of acetone-water solutions: on the scattering curves the first principal maximum was not resolved, whereas it was resolved on the curve obtained by simple summation.

In this connection we may mention investigations on two-component sodium and potassium silicate glasses carried out by the Raman spectrum method at the Institute of Silicate Chemistry by Kolesova [13]. These results confirmed that, in these glasses, regions of heterogeneity of the order of 100 A and more in diameter, such as are present in sodium borosilicate glasses, are absent. Variations with composition of the frequencies and intensities of certain bands in the spectrum are to be expected if the regions of chemical heterogeneity are small enough for atoms in one region to effect the vibrations of atoms in another, which is in accord with the presence of the "boundary effect" that we detected by X-rays. Similar results are obtained for borosilicate glasses: porous glasses prepared from these were investigated by one of the present authors by sorption methods, and it was found possible to estimate the radii of the pores, which were found to be about 10 A. These results were confirmed in an investigation of the same glasses by the method of low-angle scattering of X-rays.

All these facts, and all the variety of experimental material obtained in the study of many complex glasses by various methods of physicochemical analysis [7, 14-23], have convinced us of the fruitfulness of the concept of the microheterogeneous structure of complex glasses- of the existence in them of "chemical order"- a concept that has caused many foreign investigators of the hypothesis of a disordered lattice to publish papers in recent years in which they acknowledge the need for a re-examination of the basis of this hypothesis [24-28].

The prolonged polemics between supporters of the disordered-lattice hypothesis and those of the crystallite hypothesis on the question of the degree of "physical order" in the disposition of the atoms has ended in the general development of the compromise view, according to which there are points of maximum order, which can be logically termed crystallites, in the continuous disordered lattice. Such crystallites, however, cannot be more than 10-20 A in size and have nothing in common with the regions of heterogeneity, which may be much larger. These regions themselves have continuous lattices with crystallites at particular points, and they differ among themselves in chemical composition. The development of the hypothesis of the microheterogeneous structure of complex glasses and the interpretation on its basis of the physicochemical properties of glasses – and not the continuation of the groundless dispute about the crystallite and disorder theories of structure – these form the immediate problem of the investigators of the vitreous state.

SUMMARY

1. It has been established that sodium borosilicate glasses that are capable of becoming opalescent and the porous glasses obtained from them by leaching have a common structure.

2. The light scattering and opalescence of sodium borosilicate glasses result from their differentiation into silica and borate components, and it is this differentiation that makes it possible to obtain porous products by leaching.

3. The variation in the intensity of the scattering of light by sodium borosilicate glasses is associated with the variation in the degree of dispersion of the second component, i.e. the borate component that is dispersed through the skeleton.

4. The dimensions of the chemically homogeneous regions in sodium borosilicate glasses have been estimated by a study of the structure of the corresponding porous glasses.

5. The presence of local chemical order (submicroheterogeneous structure) is characteristic not only for sodium borosilicate glasses, but also for most complex glasses.

LITERATURE CITED

[1] D. I. Levin, S. P. Zhdanov, and E. A. Porai-Koshits, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 1, 31. *

[2] S. P. Zhdanov, E. A. Porai-Koshits, and D. I. Levin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 2, 197. **

[3] E. A. Porai-Koshits, Proc. Acad. Sci. USSR 36, 285 (1942); J. Gen. Chem. 12, 196 (1942).

[4] E. A. Porai-Koshits, Doctorate thesis, Leningrad, 1953.

[5] S. P. Zhdanov, Thesis, Leningrad, 1950.

[6] D. I. Levin, Thesis, Leningrad, 1951.

---

* Consultant's Bureau Translation, p. 27.

** Consultant's Bureau Translation, p. 177.

[7] I. V. Grebenshchikov and O. S. Molchanova, J. Gen. Chem. 12, 588 (1942).

[8] A. F. Prebus, J. W. Michener, Ind. Eng. Chem. 46, 147 (1954).

[9] V. L. Indenbom, Proc. Acad. Sci. USSR 89, 509 (1953).

[10] P. Debye, A. M. Bueche, J. Appl. Phys. 20, 518 (1949).

[11] E. A. Porai-Koshits, Proc. Acad. Sci. USSR 40, 394 (1943).

[12] V. I. Danilov, A. M. Zubko, and A. I. Danilova, J. Expt. Theor. Physics 19, 242 (1949).

[13] V. A. Kolesnikova, Thesis, Leningrad, 1953.

[14] K. S. Evstropyev, Bull. Acad. Sci. USSR, Physics Series 4, 616 (1940).

[15] K. G. Kumanin, Bull. Acad. Sci. USSR, Physics Series 4, 588, (1940).

[16] O. K. Botvinkin, Bull. Acad. Sci. USSR, Physics Series 4, 600 (1940).

[17] R. Müller, C. Weinstein, Acta. Phys. Chim. USSR, 3, 465 (1935).

[18] R. Müller, P. Markin, Acta, Phys, Chim. USSR, 4, 471 (1936).

[19] R. Müller, Acta. Phys. Chim. USSR, 1, 407 (1932); 4, 99 (1936); 4, 481 (1936).

[20] R. Myuller, Bull. Acad. Sci. USSR, Physics Series 4, 607 (1940).

[21] A. M. Venderovich, V. A. Presnov, and V. I. Chernykh, Collection in Honor of the 70th Birthday of Acadamician A. F. Ioffe, 192, 1950.

[22] B. I. Markin, J. Theor. Physics 22, 932 and 941 (1952).

[23] O. A. Esin, Bull. Acad. Sci. USSR, Chem. Series No. 6, 561 (1948).

[24] W. A. Weyl, J. Soc. Glass Techn. 35, 421, 448, 462, 469 (1951).

[25] W. A. Weyl, Phase Transformations in Solids, New York and London, 1951.

[26] A. G. Smekal, J. Soc. Glass Techn. 35, 411 (1951).

[27] N. J. Kreide, Glass. Ind. 31, 573 (1950).

[28] J. M. Stevels, Philips Tech. Rund. 13, 350 (1952).

Received April 2, 1954

Institute of Silicate Chemistry of
the USSR Academy of Sciences

REACTION OF VITREOUS SODIUM SILICATES AND ALUMINOSILICATES WITH AQUEOUS SOLUTIONS

COMMUNICATION 6. REACTION OF VITREOUS SODIUM SILICATES AND ALUMINOSILICATES WITH CAUSTIC ALKALI SOLUTIONS

S. K. Dubrovo and Yu. A. Schmidt

We have previously studied the action of water and acid solutions on vitreous sodium silicates and aluminosilicates [1-4]. In alkaline solutions the mecahnism of the breakdown of these glasses is different from that in acid solutions, and such comparison that can be made with the behavior in water is to be attributed to the fact that in such a treatment an alkaline solution is formed. In treatments with water, and particularly with solutions of acids, protective silicic or aluminosilicic acid films formed on the surface of the glass play an essential part in the breakdown process by controlling the rate of ion exchange between the glass that is as yet unchanged and the solution. When sodium silicates are treated with caustic alkali solutions, either no film at all is formed, or the film formed is a porous one.

When there is no film, the rate at which the glass is broken down is no longer determined by ionic diffusion through a film, but is determined directly by the exchange of ions from the surface of the glass with ions from the solution. The rate at which the silica of the glass reacts with alkali is also to be associated with this process.

There are very few data in the literature on the interaction of vitreous sodium silicates and aluminosilicates with alkaline solutions. The work of Dimbleby and Turner [5] is noteworthy: these authors investigated the action of 2N solutions of sodium carbonate and caustic soda on sodium silicates ($Na_2O \cdot 2SiO_2$, $Na_2O \cdot 3SiO_2$ and $Na_2O \cdot 4SiO_2$) and also on aluminosilicates in which Na_2O was replaced by Al_2O_3 (over the range 0.12-0.30 of a molecular proportion) in the silicate $Na_2O \cdot 3SiO_2$. As the Na_2O content of the sodium silicates fell, their stability toward sodium carbonate solution increased greatly, whereas, their stability towards caustic soda solution changed only slightly; the first of these solutions had much the stronger disrupting action. As Na_2O was replaced in the silicate by Al_2O_3, the first portions of the aluminum oxide were more effective, succeeding portions having little effect on the stability of the glasses. From their experiments, the authors do not make any inferences relating to the mechanism of the breakdown of the glasses by alkaline solutions.

In the present investigation we have studied the character of the interaction of vitreous sodium silicates and aluminosilicates with solutions of caustic alkali. With this object we have investigated the breakdown produced by caustic alkali solutions of various concentrations in sodium silicates of composition in the range $Na_2O \cdot 1.4SiO_2$ to $Na_2O \cdot 6SiO_2$, and also in quartz glass and in sodium aluminosilicates consisting of sodium disilicate with additions of 0.05-1 molecular proportion of aluminum oxide. As in previous investigations, the breakdown of the glasses was characterized by the amount in moles of the oxides that passed into solution from 1 sq. cm of glass surface (n_{Na_2O}, n_{SiO_2} and $n_{Al_2O_3}$).

EXPERIMENTAL

Reaction of Vitreous Sodium Silicates with Caustic Alkali Solutions. In order to determine the dependence of the tendency for sodium silicates to undergo breakdown on their silica contents and on the pH of the solution, experiments were carried out on eight sodium silicates treated in caustic soda solutions varying in concentration from 0.01 to 3 N. Also, the stabilities of powdered quartz glass and sodium disilicate after acid treatment were determined. After the leaching treatment, the disilicate contained 81.2% SiO_2, 0.54% Na_2O, and 18.3% H_2O [6]. In view of the fact that the properties of the acid-treated sodium silicate powder should be similar in properties to the siliceous film formed on the surface of this silicate, a study of the rate of solution of this powder was of some interest. The test specimens of sodium silicate were in the form of disks, 10-12 sq. cm in area. The powders of quartz glass and treated sodium disilicate had a grain size of 140-200μ. The results of the tests on these were also related to 1 sq. cm of surface, this being effected by calculation. The experiments were carried out at 40° in a silver apparatus.

TABLE 1

Reaction of Vitreous Sodium Disilicate with Caustic Soda Solutions

Solution	Index	Time (hours)					
		0.5	1	2	4	6	8
Water	$n_{Na_2O} (\times 10^{-6})$	11	18	30	47	62	76
	$n_{SiO_2} (\times 10^{-6})$	2.3	3.2	4.2	5.8	9.3	13
	a	0.10	0.09	0.07	0.06	0.08	0.09
0.01 N NaOH	$n_{Na_2O} (\times 10^{-6})$	7.0	11	21	40	59	–
	$n_{SiO_2} (\times 10^{-6})$	2.7	4.7	11	39	72	–
	a	0.19	0.21	0.26	0.49	0.60	–
0.01 N KOH	$n_{Na_2O} (\times 10^{-6})$	–	4.9	12	28	50	64
	$n_{SiO_2} (\times 10^{-6})$	–	2.7	7.9	39	72	109
	a	–	0.24	0.32	0.70	0.72	0.84
0.1 N NaOH	$n_{Na_2O} (\times 10^{-6})$	3.2	4.8	7.7	15	24	–
	$n_{SiO_2} (\times 10^{-6})$	4.6	7.9	15	31	49	–
	a	0.72	0.82	0.97	1.0	1.0	–
1.0 N NaOH	$n_{Na_2O} (\times 10^{-6})$	0.09	0.17	0.33	0.5	0.70	–
	$n_{SiO_2} (\times 10^{-6})$	0.18	0.35	0.67	1.1	1.4	–
	a						

The amount of SiO_2 passing into solution was determined, as before, by a colorimetric method. The amount of Na_2O passing into solution ion in the experiments with 0.01–0.1 N solutions of caustic soda was determined from the change in the titer of the solution, change in concentration due to evaporation being taken into account. For N NaOH the determination of Na_2O was not carried out, and the values of n_{Na_2O} given in the table were calculated from n_{SiO_2}, since, on the basis of the 0.1 N NaOH experiments, it could be assumed that in this experiment dissolution of the glass occurred. In experiments with caustic potash solution, Na_2O was determined colorimetrically. The results are given in Tables 1 and 2, and also in Figures 1 and 2. For comparison, results obtained previously [1] for the reaction of the same sodium silicates with water are also given.

Table 1, which relates to the reaction of vitreous sodium disilicate with caustic alkali solution for various times, shows that the amount of Na_2O passing into solution diminishes as the concentration of alkali increases. In weakly alkaline solution (up to 0.1 N), the passage of SiO_2 into solution lags behind that of Na_2O, so that a siliceous film remains on the surface of the sodium disilicate (a i.e. the fraction of the SiO_2 originally present in the reacting layer of glass which has passed into solution is less than unity).

Dissolution of the residual siliceous film greatly increases as we pass from water to 0.01 N NaOH. In experiments with 0.1 N NaOH the value of n_{SiO_2} is increased in comparison with the value in weaker solutions only while a siliceous film remains on the surface. When, however, the film has disappeared as a result of complete dissolution, the amounts of SiO_2 going into solution are less than in the 0.01 N NaOH experiments. This is even more marked when we pass to N NaOH, when dissolution of the glass appears to occur right from the start of the treatment. The rate at which SiO_2 passes from the sodium disilicate into solution is then much less in comparison with the behavior in less concentrated solutions. In a treatment with 0.01 N KOH, the rate of breakdown of the sodium disilicate is less at the beginning of the experiment than it is in the caustic soda solution of the same concentration. In the course of time, however, this difference disappears. With respect to the rate at which Na_2O passes into solution, breakdown of the siliceous film is appreciably more rapid in the caustic potash solution, a fact that can be deduced from a comparison of the values of a.

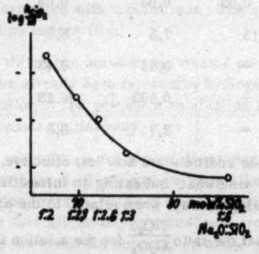
The data in Table 2 characterize the breakdown of sodium silicates and quartz glass by caustic soda solutions. In the case of the silicate $Na_2O \cdot 1.4SiO_2$, simple treatment with water results almost in the dissolution of the glass, and no siliceous film is formed on the surface. As the concentration of alkali increases, the amount of SiO_2 passing into solution falls rapidly. For the silicate $Na_2O \cdot 1.7\ SiO_2$, transition to dissolution occurs only when the caustic soda solution is increased to 0.01 N, and there is an associated increase in n_{SiO_2} in comparison with water. With further increase in the alkali concentration, the value of n_{SiO_2} again begins to fall. As we saw above, a similar picture is observed for sodium disilicate. With increase in the silica content of the sodium silicate, n_{SiO_2} falls as can be seen from Fig. 1. The relation of the amount of SiO_2 passing into solution to the silica content is expressed by a smooth curve, as can beseen in the experiments with 0.1 N NaOH, taken as an example (Fig. 1).

TABLE 2

Tendency for Vitreous Sodium Silicate and Quartz Glass to undergo Breakdown in Caustic Soda Solutions (Duration of treatment 1 hour)

Concentration of solution	Index	Molar ratio $Na_2O : SiO_2$								Quartz glass
		1 : 1.4	1 : 1.7	1 : 2	1 : 2*	1 : 2.3	1 : 2.6	1 : 3	1 : 6	
Water	n_{Na_2O} ($\times 10^{-6}$)	439	51	18	–	9.1	–	1.6	0.30	–
	n_{SiO_2} ($\times 10^{-6}$)	605	33	3.2	0.15	0.24	–	0.04	0.009	–
0.001 N NaOH	n_{SiO_2} ($\times 10^{-6}$)	–	–	–	0.85	–	–	–	–	0.003
0.01 N NaOH	n_{Na_2O} ($\times 10^{-6}$)	–	56	11	–	–	–	–	–	–
	n_{SiO_2} ($\times 10^{-6}$)	–	99	4.7	5.8	–	–	–	–	0.009
0.1 N NaOH	n_{Na_2O} ($\times 10^{-6}$)	–	–	4.8	–	–	–	–	–	–
	n_{SiO_2} ($\times 10^{-6}$)	210	36	7.9	9.2	1.25	0.17	0.12	0.16	0.024
1.0 N NaOH	n_{SiO_2} ($\times 10^{-6}$)	14	1.3	0.35	24	–	–	0.06	–	0.055
3.0 N NaOH	n_{SiO_2} ($\times 10^{-6}$)	–	–	–	–	–	–	0.04	–	0.083

* treated powder.



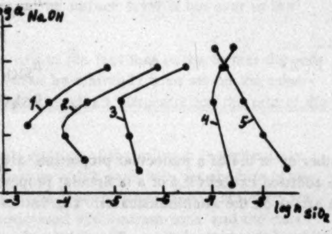


Fig. 1. Dependence on the composition of the glass of the amount of silicic acid passing into solution during a 6-hour treatment of vitreous sodium silicates with 0.1 NaOH (the values of n_{SiO_2} are based on the SiO_2 content of the glass when its composition is expressed in the form $Na_2O \cdot mSiO_2$).

Fig. 2. Dependence on the activity of NaOH of the amount of silicic acid passing into solution during a one-hour treatment of vitreous sodium silicates and quartz glass with caustic soda solutions: 1-$Na_2O \cdot 1.4SiO_2$; 2- $Na_2O . 1.7SiO_2$; 3- $NaO_2 \cdot 2SiO_2$; 4- $Na_2O \cdot 3SiO_2$; 5- quartz glass.

The rate of solution for powders of treated sodium disilicate and quartz glass increases continuously as the alkali concentration increases. The value of n_{SiO_2} for the first is 300-600 times as great as that for the second.

Reaction of Vitreous Sodium Aluminosilicates with Solutions of Caustic Alkalis. A study was made of the action of 0.1 N NaOH on six aluminosilicates prepared by the addition of aluminum oxide to sodium disilicate. We estimated the extent and character of the breakdown by the amounts of Al_2O_3 and SiO_2 that passed into solution (which were determined colorimetrically) and by the ratio of the amounts in the solution expressed as $\gamma = n_{SiO_2} / n_{AlO_3}$. The results are given in Table 3.

It will be seen from these results that the first additions of aluminum oxide to sodium disilicate greatly reduce the amounts of SiO_2 passing into solution. When the alumina content of the investigated aluminosilicates is increased

TABLE 3

Reaction of Sodium Aluminosilicates with 0.1 N Caustic Soda at 40°

Molar proportions $Na_2O : Al_2O_3 : SiO_2$	Ratio $\frac{SiO_2}{Al_2O_3}$ in original glass	Index	Time (hours)				
			1	2	4	6	8
1:2	–	$n_{SiO_2} (\times 10^{-6})$	7.9	15	31	49	53
1 : 0.05 : 2	40	$n_{SiO_2} (\times 10^{-6})$	0.18	0.75	1.47	2.24	3.10
		$n_{Al_2O_3} (\times 10^{-6})$	0.01	0.02	0.04	0.054	0.075
		γ	18	38	37	41	41
1 : 0.15 : 2	13.3	$n_{SiO_2} (\times 10^{-6})$	–	0.42	0.57	0.76	0.93
		$n_{Al_2O_3} (\times 10^{-6})$	0.01	0.01	0.02	0.03	0.035
		γ	–	42	28	25	27
1 : 0.25 : 2	8	$n_{SiO_2} (\times 10^{-6})$	0.17	0.26	0.40	0.51	0.52
		$n_{Al_2O_3} (\times 10^{-6})$	0.014	0.023	0.032	0.038	0.053
		γ	12.1	11.3	12.5	13.4	9.8
1 : 0.40 : 2	5	$n_{SiO_2} (\times 10^{-6})$	0.08	0.11	0.18	0.22	0.25
		$n_{Al_2O_3} (\times 10^{-6})$	0.01	0.02	0.025	0.037	0.047
		γ	8	5.5	7.2	6.0	5.3
1 : 0.50 : 2	4	$n_{SiO_2} (\times 10^{-6})$	0.19	0.26	0.30	0.43	0.45
		$n_{Al_2O_3} (\times 10^{-6})$	0.019	0.02	0.04	0.05	0.074
		γ	10	13	7.5	8.6	6.1
1 : 1 : 2*	2	$n_{SiO_2} (\times 10^{-6})$	–	–	0.35	0.43	0.51
		$n_{Al_2O_3} (\times 10^{-6})$	–	–	0.093	0.13	0.16
		γ	–	–	3.7	3.3	3.2

further up to 0.4 of a molecular proportion, although n_{SiO_2} again falls the additions are now less effective, and when the addition exceeds 0.4 of a molecular proportion, n_{SiO_2} begins to rise somewhat, indicating an intensification of the attack on the aluminosilicates. The values of $n_{Al_2O_3}$ vary in an analogous way, when related to the alumina content of the original glass. The values of γ given in Table 3 show that the ratio $\frac{SiO_2}{Al_2O_3}$ for the solution is not the same as for the original glass. For all of the aluminosilicates investigated, with the exception of that containing 0.05 of a molecular proportion of Al_2O_3, this ratio is higher for the solution than for the glass. Consequently, the surface of the aluminosilicates becomes enriched in aluminum ions. We have previously observed a similar phenomenon for the reaction of sodium aluminosilicates with water [3]. It is possible that the enrichment of the surface in aluminum ions is the result of a secondary process – adsorption of aluminum ions passing into solution by the residual alumina-silica layer.

DISCUSSION OF RESULTS

In our previous investigations [6] we have concluded that, when a siliceous film is present on the surface of a vitreous sodium silicate, increase in the alikali content of the solution (i.e. increase in the concentration of sodium ions and reduction in the concentration of hydrogen ions) should result in an increase in the concentration of sodium ions in the film at its boundary with the solution. As a result, the sodium ion concentration gradient in the film is reduced, and therefore also the rate of diffusion of sodium ions through the film into the solution. As the alkali concentration increases (in the sodium disilicate experiments, up to about 0.1 N), a point is reached at which complete dissolution of the siliceous film on the glass surface will occur. The rate at which sodium ions pass into solution will then be determined directly by the ion-exchange process at the glass surface. It is here necessary to remember that the experimentally observed rate of passage of sodium ions from the glass into solution (v_{Na^+}) is essentially the difference between the actual rates of transfer in the two directions:

---

* In the glass 1 : 1 : 2 there were small regions containing crystalline occlusions.

$$v_{Na^+} = v_{Na^+}' - v_{Na^+}'' = v_{H^+}$$

(v_{Na} is the rate at which sodium ions pass from glass to solution, v_{Na^+}'' is the rate at which they pass in the opposite direction, and v_H is the rate at which hydrogen ions pass into the glass). Since the sodium ion concentration is high in strongly alkaline solutions and the hydrogen ion concentration is very low, in such solutions the rate at which sodium ions pass from solution to glass (v_{Na^+}'') will probably differ only slightly from the rate of their passage into solution (v_{Na^+}'). The probability of the passage of hydrogen ions into the glass, which is proportional to their concentration, is very low, so that the velocities v_{Na^+} and v_{H^+} are also low. Increase in the concentration of alkali results in a considerable reduction in the rate at which hydrogen ions pass into the galss, and therefore also in v_{Na^+}.

As will be seen from the results of the experiments, when the alkali concentration is increased, the rate at which silica passes from sodium silicates into solution increases only while there is a residual siliceous film on the surface. When, however, this film has dissolved, the rate at which silica passes into solution falls as the alkali concentration rises. If, under these circumstances, dissolution of the silica of the glass were an independent process, increase in the alkali concentration would result in a continuous increase in the rate at which SiO_2 passes into solution, and therefore also in the rate at which Na_2O passes into solution. The behavior observed is in fact the reverse of this. It may therefore be assumed that, in the interaction of vitreous sodium silicates with strongly alkaline solutions, the rate at which the silica of the glass is dissolved depends on the rate of the primary process of exchange of sodium ions for hydrogen ions from the solution. The entry of hydrogen ions (probably more exactly, H_3O^+) probably facilitates the addition of water at one of the Si – O – Si linkages of a neighboring silicon-oxygen tetrahedron and, under alkaline conditions, this is a stimulus to the complete breakaway of this tetrahedron from the glass surface. It is probable that such a breakaway occurs immediately after the addition of a hydrogen ion to the SiO_4 tetrahedron, so that there is always a fresh glass surface in reaction with the solution, and it is almost completely saturated with sodium ions. The hydrogen ion concentration in the surface layer is however so low that there is no surface film.

The difference between the treated powder and the fresh surface lies in the fact that in the former the sodium ions have already been replaced by hydrogen ions. In this way conditions have already been set for the subsequent dissolution of the powder in an alkaline medium, so that with increase in alkali concentration the rate of dissolution increases continuously.

The reduction in the rate of dissolution with increase in the alkali content of the solution is particularly notable for sodium disilicate and for more alkaline silicate, i.e. for glasses in which each SiO_4 tetrahedron is associated, on the average, with not less than one sodium ion. In the case of the silicate $Na_2O \cdot 3SiO_2$, however, we may suppose that silicon-oxygen tetrahedra are present which are not associated with sodium ions, and the maximum on the curve for the dependence of the rate at which SiO_2 passes into solution on the alkali concentration is much more poorly defined. The rate at which quartz glass dissolves increases continuously with increase in alkali concentration. It may therefore be supposed that the rates of dissolution of silicon-oxygen tetrahedra associated in the glass with sodium ions and of those united only with other SiO_4 tetrahedra depend in different ways on the alkali concentration. The breakaway of tetrahedra of the first kind from the surface will probably occur, under the given conditions, soon after the passage of the associated sodium ions into solution, so that with increase in alkali concentration and reduction in v_{Na^+} there will be a reduction in the rate at which the tetrahedra pass into solution. On the other hand, the rate of dissolution of the SiO_4 tetrahedra that are not associated with sodium ions will rise continuously with increase in alkali concentration, as can be seen from the behavior of quartz glass. The mechanism of this process is not yet altogether clear, but it is probable that in this case also an essential part is played by the presence on the surface of quartz glass of Si — OH groups capable of taking part in ion exchange.

It is of interest also to compare the rates at which quartz glass and acid-treated sodium disilicate powder dissolve in alkalis. Since the degree of polymerization of silica in sodium disilicate is lower than in quartz glass, its silicon-oxygen skeleton will undergo appreciable hydration when treated with acid. It is to be expected that the reactivity of such a powder will be considerably higher than that of quartz glass, and this is confirmed by comparison of the values of n_{SiO_2}.

In the light of these considerations it is possible to explain also the results of the experiments of Dimbleby and Turner [5] mentioned above on the determination of the stabilities of sodium silicates in caustic soda and sodium carbonate solutions. The higher rate at which these silicates are broken down in the sodium carbonate solution is probably to be associated with the fact that in this solution the hydrogen ion activity is higher and the sodium ion activity lower than in the caustic soda solution.

As can be seen from the data in Table 2 and Fig. 1, with increase in the silica content of the silicates, the rate at which they are broken down in alkali solutions falls. This indicates that in the present case the degree of polymerization of silica in the silicon-oxygen skeleton of the glass is one of the main factors determining the rate of breakdown.

In comparing the destructive effects of caustic soda and caustic potash solutions on sodium disilicate, we have found that in the course of time the difference in the rate at which sodium ions pass from the glass to the solution disappears. This phenomenon is probably associated with the presence on the surface of the sodium disilicate of a siliceous film that controls the rates at which sodium and potassium ions diffuse. As can be seen from the data in Table 1, in the course of time the siliceous film is largely broken down (α increases), and the process of ionic diffusion through the film gradually loses its determining role.

An examination of the results obtained on the tendency for the investigated aluminosilicates to be broken down in caustic alkali solutions shows that small additions of aluminum oxide to sodium disilicate have a greater effect in improving alkali-stability than the equivalent additions of silica. For example, the stability of the aluminosilicate $Na_2O \cdot 0.15Al_2O_3 \cdot 2SiO_2$ to an eight-hour treatment in 0.1 N NaOH was found to be ten times as high as that of the corresponding silicate $Na_2O \cdot 2.3SiO_2$ (see Tables 2 and 3). With further increase in the alumina content, the rate of the dissolution of the aluminosilicates is now reduced to a lesser extent, and, beginning from the composition $Na_2O \cdot 0.5Al_2O_3 \cdot 2SiO_2$, it even rises somewhat. Here we see the influence of the previously noted effect of the depolymerization of the silicon-oxygen part of the glass skeleton as the aluminum oxide content increases. Thus, in the examination of the alkali-stability of vitreous sodium aluminosilicates it is again necessary to take into consideration the degree of polymerization of silica in the original glass.

SUMMARY

1. A study has been made of the interaction with caustic alkali solutions of sodium silicates in the range $Na_2O \cdot 1.4SiO_2 - Na_2O \cdot 6SiO_2$, of vitreous silica, and of sodium aluminosilicates consisting of sodium disilicate with an addition of 0.05-1 molecular proportion of aluminum oxide.

2. With increase in alkali concentration, the rate at which sodium ions pass into solution from the investigated silicates diminishes. The rate at which SiO_2 passes into solution increases while a residual siliceous film still remains on the surface. However, after the dissolution of this film, the rate at which the silica of the glass passes into solution diminishes as the alkali concentration increases.

3. As the silica content of silicate glasses increases, their tendency to undergo breakdown in solutions of caustic alkalis is reduced.

4. Small additions of alumina to vitreous sodium disilicate are more effective in increasing alkali-stability than equivalent additions of silica. When, however, the molecular proportion of alumina is increased to 0.5 or more, the rate of breakdown of the aluminosilicate increases somewhat, probably owing to depolymerization of the silicon-oxygen part of the skeleton.

LITERATURE CITED

[1] S. K. Dubrovo and Yu. A. Shmidt, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, No. 4, 597 (T.p.535*),

[2] S. K. Dubrovo, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No. 2, 244. ** (T.p. 197)*.

[3] Yu. A. Shmidt, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 5, 778.

[4] S. K. Dubrovo, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No. 5, 770.

[5] V. Dimbleby, W. E. S. Turner, J. Soc. Tech. 10, 304 (1926).

[6] Yu. A. Schmidt, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No. 2, 236.(T.p.191)*.

Received June 30, 1954

Institute of Silicate Chemistry of the
USSR Academy of Sciences

---

* T.p. = Consultant's Bureau Translation pagination.

SYSTEMS CONTAINING HYDROGEN PEROXIDE AT HIGH CONCENTRATION

COMMUNICATION 9. THE TERNARY SYSTEM $LiOH - H_2O_2 - H_2O$

S. Z. Makarov and T. A. Dobrynina

Unlike the peroxide compounds of sodium, potassium, rubidium, and cesium, of which the literature reports a number of the types M_2O_2 and M_2O_4 or MO_2 together with perhydrate and hydroperoxide forms, the lithium compounds are confined to lithium peroxide Li_2O_2 and the compound that it forms with hydrogen peroxide and water, the structure of which has been the subject of dispute in the literature. It has not yet been found possible to prepare lithium peroxide by the action of oxygen at high pressure and temperature on metallic lithium [1], lithium oxide [2], or lithium hydroxide [3].

The principal method for the preparation of Li_2O_2 is that of de Forcrand [1], which consists in the action of hydrogen peroxide on an aqueous-alcoholic solution of lithium hydroxide. Under these conditions de Forcrand obtained a compound of composition $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$, which yielded anhydrous Li_2O_2 when vacuum-dried over P_2O_5 for four weeks. According to Pierron [4] and Winternitz [5], lithium peroxide can be prepared directly in the anhydrous form by the action of hydrogen peroxide on lithium hydroxide in a medium of boiling alcohols. In 1952 Cohen [6] prepared a peroxide compound of lithium by the action of hydrogen peroxide on lithium ethoxide, and he characterized it as a compound of the hydroperoxide type and assigned it the formula $LiOOH \cdot H_2O$. Cohen denies the existence of perhydrate forms of lithium peroxide ($Li_2O_2 \cdot xH_2O_2 \cdot y\ H_2O$).

Thompson and Kleinberg [7] consider that a higher lithium peroxide LiO_2 exists. By rapid oxidation of a solution of lithium in liquid ammonia at $-78°$ they succeeded in obtaining a lemon-yellow precipitate, the absorption spectrum of which was found to be analogous to the absorption spectra of the higher peroxides of sodium and potassium, but there has been no further confirmation of the existence of the compound LiO_2. According to the X-ray investigations of Feher [8], Aguzzi and Genoni [9], and Cohen [6], Li_2O_2 crystallizes in the tetragonal syngony. In later work Feher [10] considers that it crystallizes in the hexagonal syngony. The density of Li_2O_2 is d^{25} 2.26 according to Cohen [6] and d^{28} 2.297 according to Feher [10].

The properties of the compounds $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$ and $LiOOH \cdot H_2O$ or $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ have received little study. In spite of de Forcrand's work, Cohen and Feher deny the existence of the first compound. According to Cohen [6], $LiOOH \cdot H_2O$ crystallizes in the rhombic syngony and has a density of d^{25} 1.69.

EXPERIMENTAL

Experimental Procedure

In order to resolve the question of the actual composition and nature of the peroxide compounds of lithium we have undertaken a systematic study of the solubility isotherms of the ternary system $LiOH - H_2O_2 - H_2O$, in which we have determined the compositions of the solid phases by the residue method at +10°, 0°, −10°, and −21°. As starting materials we used $LiOH \cdot H_2O$ free from Li_2CO_3, which was prepared by the action of water on lithium in an atmosphere of hydrogen, and concentrated hydrogen peroxide freed from stabilizers by vacuum distillation in a laboratory apparatus.

For the determination of the solubility isotherms, constant temperature was attained with the aid of a thermostat consisting of a one-liter Dewar vessel mounted in a ten-liter Dewar vessel. A thermostat of this construction was found to maintain a temperature constant within 0.3-0.5° for not less than four hours, which was quite long enough for the establishment of equilibrium in the system $LiOH - H_2O_2 - H_2O$. Cooling to the required temperature was carried out with water (+ 10°), ice (0°), a 3 : 7 mixture of KCl and ice (−10°), or a mixture of NaCl and ice (−21°).

Samples were taken in a vessel consisting of a test tube with an exit tube in which a funnel carrying a No. 3 glass filter was fixed with the aid of a rubber stopper. When the samples were taken, this vessel was placed in a Dewar vessel containing a suitable cooling mixture.

The liquid phase and the solid residue were analyzed for their contents of active oxygen and Li_2O. Weighed samples for active-oxygen determination were first stabilized in a saturated solution of boric acid, and active oxygen was subsequently determined by titration with 0.1 N $KMnO_4$ in presence of H_2SO_4. Weighed samples for Li_2O determination were transferred with the aid of water into conical flasks and boiled for 10-15 minutes to destroy H_2O_2, after which Li_2O was determined by titration to phenolphthalein with 0.1 N H_2SO_4.

For each temperature a preliminary determination was made by the graphical method of the time required for the establishment of equilibrium (from the constancy of the active-oxygen content of the liquid phase). It was found that in the system $LiOH - H_2O_2 - H_2O$ at temperatures in the range +10° to −21° equilibrium is attained, for practical purposes, within 1.5-2 hours.

Data for the Construction of the Solubility Isotherms of the Ternary System $LiOH - H_2O_2 - H_2O$

Data for the construction of the + 10°, 0°, −10°, and −21° solubility isotherms of the system $LiOH - H_2O_2 - H_2O$ are given in Tables 1-4 and are represented graphically on diagrams in Figures 1-4, and also in rectangular coordinates in Figures 5-8, in which the H_2O_2 content is plotted as abscissas and the Li_2O content as ordinates (as percent in the liquid phase).

The +10°, 0°, −10°, and −21° isotherms indicate the existence of the following solid phases: $LiOH \cdot H_2O$, $H_2O_2 \cdot 3H_2O$, $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ and $Li_2O_2 \cdot 2H_2O_2$ (the solid phase $LiOH \cdot H_2O$ is absent at −21°).

The −21° isotherm is bounded by a region of frozen solutions in the H_2O_2 concentration range of 0-20.69%.

For the other temperatures studied, the region of existence of the solid phase $LiOH \cdot H_2O$ corresponds to the following ranges of H_2O_2 concentration in the liquid phase:

Temperature	+10°	0°	−10°
Concentration of H_2O_2 in the liquid phase (% by weight).	0−4.78	0−4.59	0−4.57

The most interesting solid phases of the system are the compounds of the peroxide type $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$, $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$, and the compound $Li_2O_2 \cdot 2H_2O_2$, which has not been reported previously.

TABLE 1

Solubility Data for the system $LiOH - H_2O_2 - H_2O$ at 10°

Point No.	Composition of liquid phases (% by weight)				Composition of solid residue (% by weight)			Composition of solid phases
	0.5 O_2	H_2O_2	Li_2O	H_2O	0.5 O_2	Li_2O	H_2O	
26	0.97	2.06	7.03	92.00	0.26	32.50	67.24	$LiOH \cdot H_2O$
27	1.78	3.78	7.27	90.95	0.54	27.88	71.58	Ditto
9	2.06	4.38	7.33	90.61	2.56	31.34	66.01	Ditto
24	2.25	4.78	8.07	89.68	7.42	28.64	63.94	$LiOH \cdot H_2O + Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$
18	2.20	4.68	7.69	90.11	9.79	15.31	74.90	Ditto
8	2.44	5.19	7.27	90.29	7.84	10.83	81.33	$Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$
1	3.34	7.10	3.92	92.74	20.71	20.55	58.74	Ditto
6	3.20	8.29	3.35	92.75	17.62	15.45	66.93	Ditto
20	4.30	9.14	3.56	92.14	16.21	15.30	68.59	Ditto
3	7.33	15.58	4.04	88.63	22.25	22.54	55.21	Ditto
23	12.40	26.36	4.55	83.05	30.91	18.17	60.92	Ditto
4	14.54	0.91	4.92	80.54	24.77	22.08	53.15	Ditto
25	19.65	41.78	5.57	74.78	23.10	19.27	57.36	Ditto
7	19.14	40.69	5.48	75.38	23.31	15.13	61.56	$Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$
13	20.52	43.63	5.47	74.01	23.85	16.59	59.56	Ditto
5	22.32	47.45	5.56	72.12	26.66	20.45	52.89	Ditto
11	24.18	51.41	5.62	70.20	25.96	15.78	58.26	Ditto
28	26.48	56.30	5.94	67.58	26.81	19.38	59.81	Ditto
16	27.55	58.57	6.02	66.43	27.56	15.56	56.88	Ditto
29	26.91	57.21	5.81	67.28	29.30	16.08	54.62	$Li_2O_2 \cdot H_2O_2 \cdot 2H_2O + Li_2O \cdot 2H_2O_2$
15	27.48	58.42	5.55	66.97	35.15	15.41	49.44	$Li_2O_2 \cdot 2H_2O_2$
22	27.53	58.53	5.68	66.79	40.07	15.49	44.44	Ditto
17	30.30	64.42	5.16	64 54	36.75	12.17	51.08	Ditto
10	30.50	64.84	5.00	64.50	37.50	12.27	50.23	Ditto

TABLE 2

Solubility Data for the System $LiOH - H_2O_2 - H_2O$ at 0°

Point No.	Composition of liquid phase (% by weight)				Composition of solid residue (% by weight)			Composition of solid phases
	$0.5\ O_2$	H_2O_2	Li_2O	H_2O	$0.5\ O_2$	Li_2O	H_2O	
19	1.49	3.17	7.38	91.13	0.36	30.51	69.13	$LiOH \cdot H_2O$
16	1.75	3.72	7.22	91.03	0.51	30.03	69.46	Ditto
15	2.13	4.53	7.42	90.35	1.36	32.47	66.17	Ditto
21	2.16	4.59	7.30	90.54	7.26	13.47	79.27	$LiOH \cdot H_2O + Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$
20	3.82	8.12	4.18	92.00	9.89	9.12	80.99	$Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$
24	3.57	7.59	3.59	92.84	11.89	11.87	76.24	Ditto
1	6.43	13.67	3.85	89.72	21.89	19.59	58.52	Ditto
26	11.11	23.62	4.33	84.56	20.60	14.57	64.83	Ditto
29	14.93	31.74	4.76	80.31	24.73	21.73	53.54	Ditto
2	17.69	37.61	5.05	77.26	24.12	19.70	56.18	Ditto
14	18.79	39.95	5.07	76.14	23.60	18.52	57.88	Ditto
30	18.41	39.14	5.19	76.40	25.22	19.59	55.19	$Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$
13	19.37	41.18	4.18	76.45	24.78	18.78	56.44	Ditto
7	20.74	44.09	4.68	74.58	25.15	19.25	55.60	Ditto
12	22.06	46.90	4.27	73.67	26.33	19.35	54.32	Ditto
25/2	24.21	52.96	6.12	68.97	26.66	17.77	55.57	Ditto
11	25.44	54.09	4.52	70.04	26.44	17.66	55.90	Ditto
3	25.46	54.13	5.94	68.60	28.70	17.54	53.76	$Li_2O_2 \cdot H_2O_2 \cdot 2H_2O + Li_2O_2 \cdot 2H_2O_2$
8	25.86	54.98	4.80	69.34	32.43	16.83	49.74	$Li_2O_2 \cdot 2H_2O_2$
9	27.39	58.23	5.00	67.61	38.62	15.66	52.48	Ditto
23	29.36	62.42	4.97	65.67	37.05	13.94	49.90	Ditto
28	31.31	66.57	3.70	64.99	37.59	13.88	48.53	Ditto
10	32.33	68.73	3.19	64.48	40.13	15.52	44.35	Ditto

TABLE 3

Solubility Data for the System $LiOH - H_2O_2 - H_2O$ at −10°

Point No.	Composition of liquid phase (% by weight)				Composition of solid residue (% by weight)			Composition of solid phases
	$0.5\ O_2$	H_2O_2	Li_2O	H_2O	$0.5\ O_2$	Li_2O	H_2O	
2	1.49	3.17	7.31	91.20	1.67	31.34	66.99	$LiOH \cdot H_2O$
1	2.15	4.57	7.80	90.05	2.44	22.75	74.31	Ditto
18	1.98	4.21	7.76	90.26	4.88	22.00	73.12	$LiOH \cdot H_2O + Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$
7	2.34	4.97	7.05	90.61	8.99	20.94	70.07	Ditto
22	2.37	5.04	5.08	92.55	12.25	13.78	73.97	$Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$
8	2.54	5.40	5.68	91.78	12.29	13.25	74.46	Ditto
3	4.50	9.57	3.42	92.08	16.40	14.93	68.67	Ditto
4	9.38	19.94	4.20	86.42	17.95	15.21	66.86	Ditto
5	14.51	30.85	4.81	80.68	21.31	17.46	61.23	Ditto
6	17.29	36.76	4.91	77.80	21.92	16.12	61.96	Ditto
11	18.68	39.71	4.77	76.55	21.19	14.92	63.89	Ditto
13	18.95	40.29	5.02	76.03	23.06	14.99	61.95	$Li_2O_2 \cdot H_2O_2 \cdot 3H_2O + Li_2O \cdot H_2O \cdot 2H_2O$
9	22.00	46.47	5.25	72.75	24.85	17.33	57.82	$Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$
19	24.05	51.13	5.37	70.58	26.83	19.71	53.46	Ditto
10	25.61	54.45	5.59	68.80	28.19	18.63	53.18	$Li_2O_2 \cdot H_2O_2 . 2H_2O + Li_2O_2 \cdot 2H_2O_2$
14	25.32	53.83	5.64	69.04	34.06	14.45	51.49	$Li_2O_2 . 2H_2O_2$
12	28.75	61.12	4.58	66.67	39.17	18.13	42.70	Ditto
21	30.55	64.95	3.92	65.53	36.74	12.26	51.00	Ditto
20	35.59	75.66	2.38	62.03	40.75	11.54	47.71	Ditto

TABLE 4

Solubility Data for the System $LiOH - H_2O_2 - H_2O$ at − 21°

Point No.	Composition of liquid phase (% by weight)				Composition of solid residue (% by weight)			Composition of solid phases
	$0.5\ O_2$	H_2O_2	Li_2O	H_2O	$0.5\ O_2$	Li_2O	H_2O	
15	10.80	22.96	4.29	84.91	–	–	100	Ice
6	9.73	20.69	3.85	86.42	17.43	13.24	69.33	$Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$
1	13.13	27.91	4.44	82.43	19.87	16.00	64.13	Ditto
12	17.06	36.27	5.09	77.85	23.52	20.28	56.20	Ditto
14	17.95	38.16	5.14	76.91	23.71	18.76	57.53	Ditto
2	17.47	37.14	4.95	77.58	24.11	18.42	57.47	$Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$
17	18.86	40.10	5.00	76.14	22.59	15.31	61.60	Ditto
16	22.94	48.77	5.12	71.94	24.60	12.53	62.87	Ditto
8	24.62	52.34	5.34	70.04	25.47	16.61	67.92	Ditto
9	26.05	55.32	5.31	68.64	27.13	12.41	60.46	Ditto
3	25.51	54.23	5.43	69.06	37.75	15.54	46.17	$Li_2O_2 \cdot 2H_2O_2$
10	26.85	57.08	6.13	67.02	34.42	12.07	53.51	Ditto
22	27.59	58.66	4.08	68.33	33.63	13.05	53.32	Ditto
21	27.90	59.32	4.01	68.09	38.10	16.37	45.53	Ditto
11	31.18	66.29	4.69	64.13	35.67	10.17	54.16	Ditto
19	31.89	67.80	2.76	65.35	39.61	12.49	47.90	Ditto
4	34.09	72.43	3.53	62.38	36.60	10.01	53.39	Ditto
18	39.49	83.96	2.24	58.27	40.38	8.81	50.81	Ditto

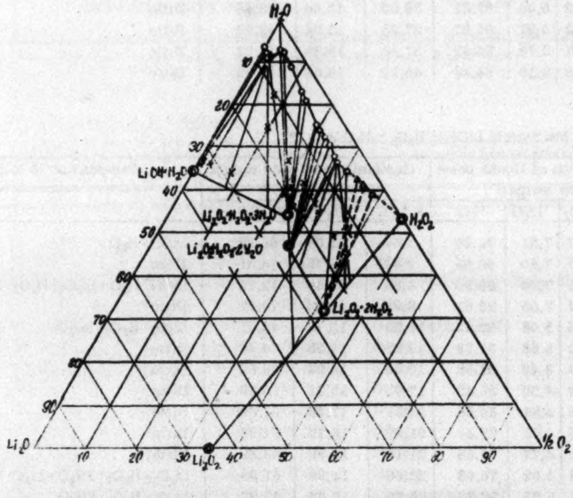


Fig. 1. + 10° isotherm of the system $LiOH - H_2O_2 - H_2O$

As the temperature is lowered, the field of existence of the compound $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$ becomes smaller. The field of existence of the solid phase $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ is at a minimum at −10°. When the temperature is raised to 0° and +10°, and also when it is lowered to − 21°, this field of existence grows somewhat larger. The solid phase $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ is least soluble at 0° (4.18-4.80% Li_2O in the liquid phase).

The diagrams in Figures 5-8 are all characterized by the presence of two clearly defined curves corresponding to the two phases $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$ and $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$.

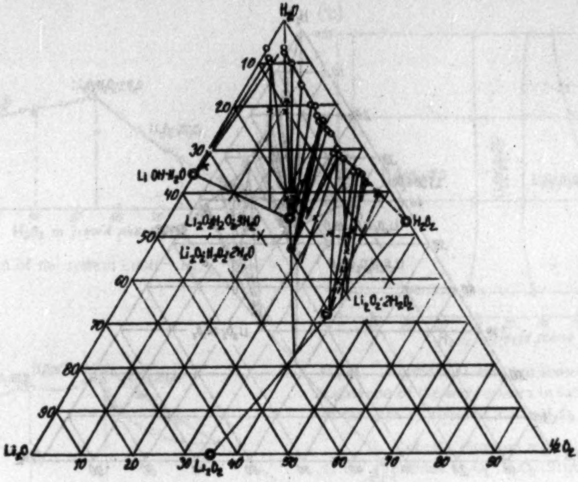


Fig. 2. 0° isotherm of the system $LiOH - H_2O_2 - H_2O$

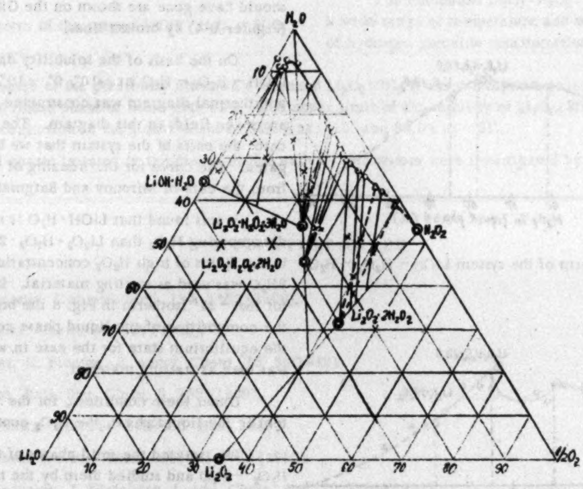


Fig. 3. −10° isotherm of the system $LiOH - H_2O_2 - H_2O$

Hence, in spite of Cohen's assertions to the contrary, we may conclude that the compounds $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$ exists.

As the temperature is lowered, the field of existence of the compound $Li_2O_2 \cdot 2H_2O_2$ becomes larger. Whereas at 10° this compound exists over a range of only 6.27% H_2O_2 (58.57-64.84% H_2O_2 in the liquid phase), at −21° its field ranges over 26.88% H_2O_2 (57.08-83.96% H_2O_2 in the liquid phase).

In the field of high H_2O_2 concentrations in the liquid phase, much decomposition occurs. Hence, the tie lines joining the liquid-phase and solid-residue compositions in the diagrams of Figures 1-4 are displaced to the right of the figurative point corresponding to the solid phase $Li_2O_2 \cdot 2H_2O_2$. The directions in which these tie lines

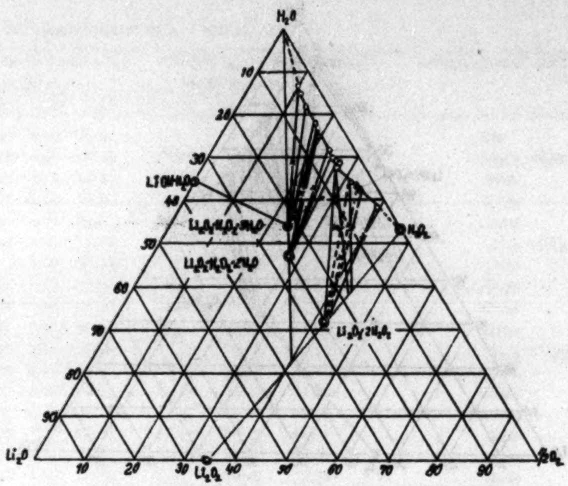


Fig. 4. −21° isotherm of the system $Li_2O_2 - H_2O_2 - H_2O$

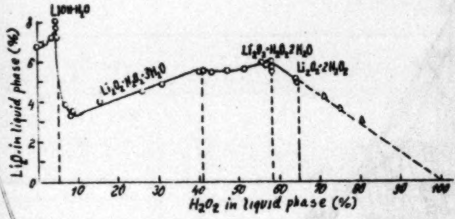


Fig. 5. + 10° isotherm of the system $LiOH - H_2O_2 - H_2O$

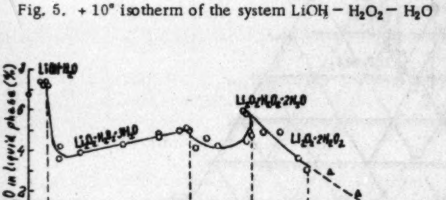


Fig. 6. 0° isotherm of the system $LiOH - H_2O_2 - H_2O$

should have gone are shown on the Gibbs triangles (Figures 1-4) by broken lines.

On the basis of the solubility data for the system $LiOH - H_2O_2 - H_2O$ at +10°, 0°, −10°, and −21°, a polythermal diagram was constructed (Fig. 9). There are seven fields in this diagram. The broken lines indicate the parts of the system that we have not investigated. The curve for the freezing of H_2O_2 was plotted from the data of Mironov and Befgman [11].

It was found that $LiOH \cdot H_2O$ is more active in decomposing H_2O_2 than $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$. Hence, in the fields of high H_2O_2 concentrations, $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ was used as starting material. In the diagram for the −21° isotherm in Fig. 8 the broken line shows the composition of the liquid phase corresponding to the equilibrium state for the case in which $LiOH \cdot H_2O$ was used as starting material.

Under these conditions, for the same Li_2O content in the liquid phase, the H_2O_2 content is less.

We isolated the solid phases of the system $LiOH - H_2O_2 - H_2O$ and studied them by the methods of physicochemical analysis.

SUMMARY

1. The ternary system $LiOH - H_2O_2 - H_2O$ was studied by the solubility method at +10°, 0°, −10°, and −21°, and solubility isotherms and polytherms were plotted for the system for the temperature range +10° to −21°.

2. A solubility study of the ternary system $LiOH - H_2O_2 - H_2O$ in which the compositions of solid phases were determined by the residue method has established the existence of the following peroxide compounds of lithium: $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$, $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ and $Li_2O_2 \cdot 2H_2O_2$.

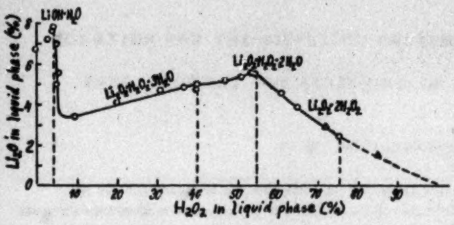


Fig. 7. − 10° isotherm of the system LiOH − H_2O_2 − H_2O

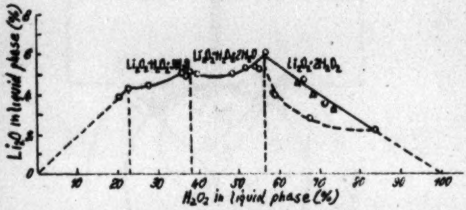


Fig. 8. −21° isotherm of the system LiOH − H_2O_2 − H_2O

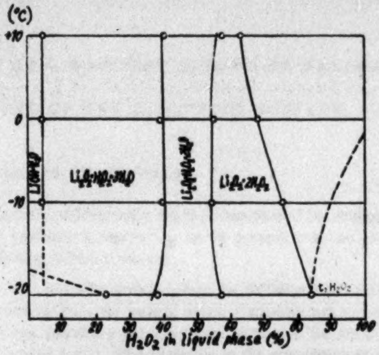


Fig. 9. Polythermal diagram showing the limits of existence of the solid phases in saturated solutions of the ternary system LiOH − H_2O_2 − H_2O

3. Cohen's assertion regarding the absence of the compound $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$, previously found by de Forcrand, was not confirmed.

The compound $Li_2O_2 \cdot H_2O_2 . 3H_2O$ exists over a wide range of temperature and over a wide range of hydrogen peroxide concentrations (5.0-40.0% H_2O_2).

4. The existence of the previously unknown compound $Li_2O_2 \cdot 2H_2O_2$ was established; it is stable at H_2O_2 concentrations in the liquid phase of more than 50%. The upper limit of the stability of $Li_2O_2 \cdot 2H_2O_2$ is at a hydrogen peroxide concentration in the liquid phase of 64.8% at +10° and 84.0% at −21°.

5. The solid phases isolated in the course of the study of this system were investigated by several physicochemical methods.

LITERATURE CITED

[1] R. deForcrand, Comptes rend. 130, 1465 (1900).

[2] J. Milbauer, Chem. 40, 587 (1916).

[3] F. Fischer, H. Ploetze, Z. anorg Chem. 75, 30(1912).

[4] P. Pierron, Bull. Soc. Chim. 6, 235 (1939).

[5] P. Winternitz, U.S. Pat. 2488485, Nov. 1949.

[6] A. J. Cohen, J. Am. Chem. Soc. 74, 3762 (1952).

[7] J. K. Thompson, J. Kleinberg, J. Am. Chem. Soc. 73, 1243(1951).

[8] F. Feher, Ang. Chem. 51, 497 (1938).

[9] A. Aguzzi, F. Genoni, Gazz. chim. Ital. 68, 816 (1938).

[10] F. Feher, Ber. 11, 1389 (1953).

[11] K. E. Mironov and A. G. Bergman, Proc. Acad. Sci. USSR 81, 6, 1081 (1951).

Received July 26, 1954

N. S. Kurnakov Institute of General and Inorganic Chemistry of the USSR
Academy of Sciences

BLANK
PAGE

EQUATION FOR THE DIFFUSION CURRENT AT A DROPPING ELECTRODE TAKING INTO ACCOUNT THE SCREENING OF PART OF THE ELECTRODE SURFACE

S. G. Mairanovsky and M. B. Neiman

In the derivation of the equation for the diffusion current in polarography the fact that part of the dropping mercury electrode is screened by the surface of the tip of the capillary is neglected. In the present paper an estimate is made of the effect of this screening on the value of the limiting diffusion current.

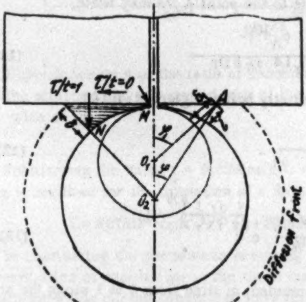


Fig. 1. Diagram for calculation of the screening effect (the left half of the screened space is shaded).

Let is be supposed that the diffusion front, extending from the surface of the electrode into the solution, reaches a point A on the surface of the tip (Fig. 1) at time $t = \tau$. The variation in the concentration of the depolarizer at this point as further time elapses will be expressed by the relation (the effect of the sphericity of the dropping electrode [1, 2] being neglected):

$$\frac{c_A}{\partial t} = D\frac{\partial^2 c_A}{\partial x^2}, \tag{1}$$

(D is the diffusion coefficient of the depolarizer and x is the distance from the surface of the drop).

In order to simplify the calculation we shall apply the concept of a conventional thickness of diffusion layer [3], equal in this case to

$$\delta = \sqrt{3/7\,\pi D t}.$$

The value of $\partial c_A/\partial x$ at A is close to zero [4], but at the electrode surface it is c_A/l [3] (l is the distance of the point A from the surface of the drop), so that the second derivative of concentration with respect to distance can be approximately expressed as

$$\frac{\partial^2 c_A}{\partial x^2} \approx -\frac{c_A}{l^2}, \text{ so that}$$

$$\left(\frac{c_A}{\partial t}\right)_A \approx -D\frac{c_A}{l^2}. \tag{2}$$

The introduction of this approximation, as will be seen later, does not affect the final results to an appreciable extent.

At $t = \tau$ the distance l is equal to the thickness of the diffusion layer δ; as time proceeds it diminishes owing to the growth of the drop. An examination of Fig. 1 indicates that

$$l = \frac{r(1-\cos\varphi)}{\cos\varphi} = \frac{2r\sin^2\frac{\varphi}{2}}{\cos\varphi}, \tag{3}$$

(r is the radius of the drop).

At low values of φ_1, for which

$$\varphi_1 \approx \sin\varphi_1 \text{ (4) and } \cos\varphi_1 \approx 1, \tag{5}$$

we may write, on the basis of Equation 3:

$$l/l_1 = \frac{r_1}{r} = \left(\frac{t_1}{t}\right)^{1/3}. \tag{6}$$

Assuming that $t_1 = \tau$, we obtain from Equation 6:

$$l = \delta\left(\frac{\tau}{t}\right)^{1/3}. \tag{7}$$

After substituting for $\underline{l}$ from Equations 7 and 2, we obtain:

$$\left(\frac{\partial c_A}{\partial t}\right)_A = -D\,\frac{c_A t^{2/3}}{\delta^2 \tau^{2/3}}\,. \tag{8}$$

which yields, after separation of variables and integration between the limits of τ and t ($\tau \leqslant t$):

$$\ln\frac{c_A}{c_0} = -{}^3/_5\,D\,\frac{t^{5/3} - \tau^{5/3}}{\delta^2 \tau^{2/3}}\,, \tag{9}$$

(c_0 is the concentration in the mass of the solution).

After substitution of the value $\delta^2 = {}^3/_7\,\pi D\tau$ in Equation 9 and rearrangement, we obtain for c_A:

$$c_A = c_0 e^{-7/5\pi\left[\left(\frac{t}{\tau}\right)^{5/3} - 1\right]}. \tag{10}$$

For the conceptration gradient at the surface of the drop opposite to the point $\underline{A}$ we may write:

$$\left(\frac{\partial c_A}{\partial x}\right)^{\text{scr.}}_{x=0} \approx \frac{c_A}{\underline{l}} = \frac{c_A t^{1/3}}{\tau^{1/3}\,{}^3/_7\,\pi D\tau}\,. \tag{11}$$

The concentration gradient at the unscreened surface (the effect of sphericity being neglected) is [4]

$$\left(\frac{\partial c}{\partial x}\right)^{\text{unscr.}}_{x=0} = \frac{c_0}{\sqrt{{}^3/_7\,\pi D\tau}}\,. \tag{12}$$

From Equations 10, 11, and 12 it follows that

$$\left(\frac{\partial c_A}{\partial x}\right)^{\text{scr.}}_{x=0} : \left(\frac{\partial c}{\partial x}\right)^{\text{unscr.}}_{x=0} = \frac{t^{5/6}}{\tau^{5/6}}\, e^{\frac{7}{5\pi}\left[\left(\frac{t}{\tau}\right)^{5/3} - 1\right]}. \tag{13}$$

We now introduce a new variable y = τ/t,, varying at a given moment of time from 0 to 1 along the arc $\underline{M}$ (Fig. 1). The graph for the dependence of the ratio of concentration gradients on $\underline{y}$ for an arbitrary moment of time is given in Fig. 2. The mean instantaneous value of the ratio of gradients over the whole of the screened surface is given by:

$$\left[\left(\frac{\partial c}{\partial x}\right)^{\text{scr.}}_{x=0} \Big/ \left(\frac{\partial c}{\partial x}\right)^{\text{unscr.}}_{x=0}\right]_{\text{mean}} = \int_{y=0}^{y=1} y^{-5/6}\, e^{-\frac{7}{5\pi}(y^{-5/3} - 1)}\, dy = M. \tag{14}$$

It follows from Equation 14 that the value of $\underline{M}$, at least on the simplifying assumptions made, is independent of time and has the value of about 0.554 (graphical integration). It may therefore be considered that the mean current density at the screened parts of the surface of the drop are little more than half of the corresponding values for the unscreened parts.

Let us derive the expression for the total current. It follows from an examination of Fig. 1 that the screened surface is

$$S_{\text{scr.}} = 2\pi r^2\,\frac{\sqrt{{}^3/_7\,\pi Dt}}{r + \sqrt{{}^3/_7\,\pi Dt}}\,. \tag{15}$$

For short periods of dropping $r \gg \sqrt{{}^3/_7\,\pi Dt}$, and Equation 15 may be expressed in the form: (15)

$$S_{\text{scr.}} \approx 2\pi r\sqrt{{}^3/_7\,\pi Dt}\,. \tag{16}$$

The expression for the current taking into account the corrections for the sphericity of the electrode [1, 2] and the reduced current density in the screened regions has the form:

$$i = nFDc_0\left(4\pi r^2 - 2\pi r\sqrt{{}^3/_7\,\pi Dt}\right)\left(\frac{1}{\sqrt{{}^3/_7\,\pi Dt}} + \frac{1}{r}\right) + 2\pi r\sqrt{{}^3/_7\,\pi Dt}\cdot nFDc_0 M\left(\frac{1}{\sqrt{{}^3/_7\,\pi Dt}} + \frac{1}{r}\right). \tag{17}$$

The first member of the expression is the component of the current at the unscreened surface, and the second is the component at the screened surface. After rearrangement, Equation 17 takes the form:

$$i = nFDc_0\cdot 4\pi r^2\left(\frac{1}{\sqrt{{}^3/_7\,\pi Dt}} + \frac{1}{r}\right)\left[1 - \frac{\sqrt{{}^3/_7\,\pi Dt}}{2r}\,(1-M)\right]. \tag{18}$$

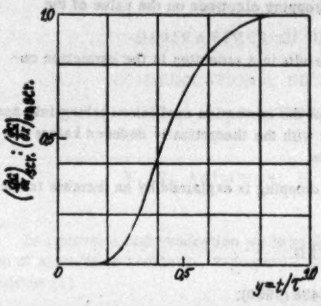


Fig. 2. Dependence on y of the ratio of concentration gradients at the screened and unscreened parts of the surface (for a given value of t)

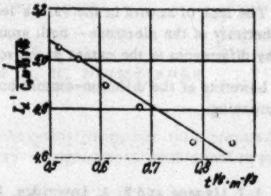


Fig. 3. Dependence of the diffusion-current constant on $t^{1/6}\, m^{-1/3}$ for a capillary working with a blade. 2.07-millimolar solution, h = 40 cm, M = 2.25, t = 0.512 sec.

Substituting the value $r = 0.026(mt)^{1/3}$, in Equation 18, opening the square brackets, and integrating over the time t_0 required for the formation of a drop, we obtain for the average current:

$$\bar{i} = 607nD^{1/2}c_0m^{2/3}t^{1/6}[1 + 39(mt_0)^{-1/3}(Dt_0)^{1/2} - 8.7(mt_0)^{-1/3}(Dt_0)^{1/2} - 35(mt_0)^{-2/3}Dt_0]. \qquad (19)$$

In considering the phenomena occurring at the screened surface, we did not take into account the fact that the concentration of depolarizer at the tip of the capillary, which is reduced during the growth of the drop, will not regain the value c_0 (the concentration in the mass of the solution) after the drop has broken away. The effect of this will be to reduce the value of M, in comparison with the value given by Equation 14, and to increase the effective screening surface.

The magnitude of this effect depends mainly on the area of the tip of the capillary and the agitation given to the solution when the drop breaks away, i.e. is determined solely by the properties of the given capillary. The displacement of impoverished solution from the screened space during the growth of the mercury drop has a similar effect. In order to take these factors into account, a correction coefficient $B \geqslant 1$ must be introduced in front of the second member within the square brackets in Equation 18, and the value of B will be different for different capillaries. The value of B is particularly high for capillaries working with a blade which effects forced breakaway of the drop [5] and which greatly increases the screened surface. Results of experiments with such a capillary are shown in Fig. 3; for this capillary the value of B was found to be about 6.

Another possible case arises when the outside of the capillary is tapered at the tip. The area of the tip is then reduced, and the screened surface is also reduced. In this case B may be less than unity. Finally, therefore, we have:

$$\bar{i} = 607nD^{1/2}c_0m^{2/3}t_0^{1/6}[1 + 39\, m^{-1/3}t_0^{1/6}D^{1/2} - B(8.7m^{-1/3}t_0^{1/6}D^{1/2} + 35\, m^{-2/3}t_0^{1/3}D)]. \qquad (20)$$

In our opinion, only variation in the value of B for different capillaries can explain the large discrepancies found experimentally by various workers in the numerical values of the coefficient A in front of the correction term of the corrected Ilkovic equation [1, 2, 6, 7].

The effect of screening can explain also the reduction in the diffusion-current constant at a low rate of dropping. This phenomenon was first pointed out by L. and T. Meites [6], who, however, could not explain it. It can be seen from Equation 19 that the last correction member is most dependent on t_0 (mt_0 is constant for a given capillary), but its value becomes appreciable only for high values of t_0. In order to take this relationship into account, Equation 15 should be used in place of 16, account being taken of the fact that at high values of t_0 the conditions expressed in Equations 4 and 5 will not apply exactly, and this will affect the value of M. This does not affect, however, the general course of the relation of the diffusion-current constant to t_0 *.

---

* After the present work was finished we became acquainted with a paper by Matsuda [8], which also takes account of screening, attributing it to the effect of reduction in the volume of the diffusion layer due to the presence therein of the end of the capillary. According to Matsuda, the effect of screening for all capillaries is to reduce the correction member for sphericity by a factor of 1.54, without change of sign.

SUMMARY

1. An estimate is made of the effect of the screening of the dropping electrode on the value of the diffusion current.

2. It is shown that screening of part of the electrode surface results in a reduction in the correction coefficient for sphericity in the corrected Ilkovic equation.

3. The lack of accord in the values foundby various authors for the correction coefficient taking into account the sphericity of the electrode – both among themselves and also with the theoretically deduced values – is explained by differences in the extent of the screening of the electrode.

4. Lowering of the diffusion-current constant at a low rate of dropping is explained by an increase in the extent of screening.

LITERATURE CITED

[1] J. J. Lingane and B. A. Loveridge, J. Am. Chem. Soc. 72, 438 (1950).

[2] H. Strehlow and M. Stackelberg Z. Elektochem. 54, 51 (1950).

[3] S. Glasstone, Introduction to Electrochemistry, Foreign Lit. Press, 1951, p. 578.

[4] A. N. Frumkin, V. S. Bagotsky, Z. A. Iofa, and V. N. Kabanov, Kinetics of Electrode Processes, Moscow State Univ. Press. Moscow, 1952, p. 87.

[5] E. M. Skobets and N. S. Kavetsky, Factory Labs; 15, 1299 (1949).

[6] L. Meites and T. Meites, J. Am. Chem. Soc. 73, 395 (1951).

[7] W. Hans and W. Jensch, Z. Elektrochem. 56, 648 (1952).

[8] H. Matsuda, Bull. 26, 342 (1953).

Received July 29, 1954

Institute of Chemical Physics of the
USSR Academy of Sciences

DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 6. DIESTERS OF 2-ISOPROPOXY-, 2-ISOBUTOXY-, AND 2-ISOPENTYLOXY-VINYLPHOSPHONIC ACIDS

K. N. Anisimov, N. E. Kolobova and A. N. Nesmeyanov

In a previous communication we have described diesters of 2-alkoxyvinylphosphonic acids prepared by the action of alcohols on 2-ethoxy-, 2-propoxy-, 2-butoxy-, and 2-hexyloxy-vinylphosphonic dichlorides in presence of pyridine [1].

We decided that, in order to make a more extensive and thorough investigation of these interesting compounds, we should carry out the synthesis of diesters of 2-isopropoxy-, 2-isobutoxy-, and 2-isopentyloxy-vinylphosphonic acids.

For the preparation of these compounds we used the method described previously, and we obtained the dimethyl, diethyl, dipropyl, diisopropyl, dibutyl, diisobutyl, diallyl, dihexyl, bis(2-methoxyethyl), and bis(2-ethoxyethyl) esters of 2-isopropoxy-, 2-isobutoxy-, and 2-isopentyloxy-vinylphosphonic acids.

The compounds so obtained are colorless liquids, readily distilled under reduced pressure, and capable of being preserved unchanged for a long time. All of the esters are soluble in the usual organic solvents; only the dimethyl, bis(2-methoxyethyl), and bis(2-ethoxyethyl) esters are soluble in water. The diallyl esters polymerize in presence of peroxides, and they will copolymerize with methyl methacrylate and other unsaturated compounds. Physical properties of the compounds obtained are given in Tables 1-3.

TABLE 1

Formula of compound	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}
$i\text{-}C_3H_7-O-CH=CHPO(OCH_3)_2$	94 – 95 (2)	1.4438	1.1042
$i\text{-}C_3H_7-O-CH=CHPO(OC_2H_5)_2$	103 (1)	1.4428	1.0450
$i\text{-}C_3H_7-O-CH=CHPO(O-C_3H_7\text{-}n)_2$	113 (1)	1.4439	1.0141
$i\text{-}C_3H_7-O-CH=CHPO(O-C_3H_7\text{-}i)_2$	99 (2)	1.4360	0.9973
$i\text{-}C_3H_7-O-CH=CHPO(O-C_4H_9\text{-}n)_2$	132 – 133 (2)	1.4460	0.9910
$i\text{-}C_3H_7-O-CH=CHPO(O-C_4H_9\text{-}i)_2$	116 (1)	1.4440	0.9847
$i\text{-}C_3H_7-O-CH=CHPO(OC_3H_5)_2$	120 (2)	1.4651	1.0448
$i\text{-}C_3H_7-O-CH=CHPO(OC_6H_{13}\text{-}n)_2$	149 (2)	1.4498	0.9628
$i\text{-}C_3H_7-O-CH=CHPO(OCH_2-CH_2-OCH_3)_2$	155 (3)	1.4555	1.1002
$i\text{-}C_3H_7-O-CH=CHPO(O-CH_2-CH_2-OC_2H_5)_2$	155 (1)	1.4520	1.0652

TABLE 2

Formula of compound	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}
$i\text{-}C_4H_9-O-CH=CHPO(OCH_3)_2$	105 (2)	1.4487	1.0831
$i\text{-}C_4H_9-O-CH=CHPO(OC_2H_5)_2$	110 (2)	1.4435	1.0310
$i\text{-}C_4H_9-O-CH=CHPO(OC_3H_7\text{-}n)_2$	124 (2)	1.4442	1.0014
$i\text{-}C_4H_9-O-CH=CHPO(OC_3H_7\text{-}i)_2$	120 (2)	1.4405	0.9948
$i\text{-}C_4H_9-O-CH=CHPO(OC_4H_9\text{-}n)_2$	144 (1)	1.4470	0.9849
$i\text{-}C_4H_9-O-CH=CHPO(OC_4H_9\text{-}i)_2$	135 (2)	1.4440	0.9804
$i\text{-}C_4H_9-O-CH=CHPO(OC_3H_5)_2$	130 (1)	1.4643	1.0417
$i\text{-}C_4H_9-O-CH=CHPO(OC_6H_{13}\text{-}n)_2$	165 (1)	1.4498	0.9597
$i\text{-}C_4H_9-O-CH=CHPO(OCH_2-CH_2-OCH_3)_2$	163 (2)	1.4543	1.0900
$i\text{-}C_4H_9-O-CH=CHPO(OCH_2-CH_2-OC_2H_5)_2$	170 (2)	1.4509	1.0533

TABLE 3

Formula of Compound	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}
$(CH_3)_2-CH-CH_2-CH_2-O-CH=CHPO(OCH_3)_2$	109.5 (1)	1.4508	1.0667
$(CH_3)_2-CH-CH_2-CH_2-O-CH=CHPO(OC_2H_5)_2$	119 (1)	1.4464	1.0928
$(CH_3)_2-CH-CH_2-CH_2-O-CH=CHPO(OC_3H_7\text{-}n)_2$	132 (1)	1.4482	0.9960
$(CH_3)_2-CH-CH_2-CH_2-O-CH=CHPO(OC_3H_7\text{-}i)_2$	120 (2)	1.4418	0.9866
$(CH_3)_2-CH-CH_2-CH_2-O-CH=CHPO(OC_4H_9\text{-}n)_2$	148 (1)	1.4490	0.9896
$(CH_3)_2-CH-CH_2-CH_2-O-CH=CHPO(OC_4H_9\text{-}i)_2$	145 (2)	1.4458	0.9734
$(CH_3)_2-CH-CH_2-CH_2-O-CH=CHPO(OC_3H_5)_2$	137 (1)	1.4645	1.0335
$(CH_3)_2-CH-CH_2-CH_2-O-CH=CHPO(O-C_6H_{13}\text{-}n)_2$	171 (1)	1.4500	0.9618
$(CH_3)_2-CH-CH_2-CH_2-O-CH=CHPO(OCH_2-CH_2-OCH_3)_2$	173 (1)	1.4550	1.0758
$(CH_3)_2-CH-CH_2-CH_2-O-CH=CHPO(OCH_2-CH_2-OC_2H_5)_2$	179 (1)	1.4527	1.0453

EXPERIMENTAL

Diesters of 2-Isopropoxyvinylphosphonic Acid

Dimethyl 2-Isopropoxyvinylphosphonate $i\text{-}C_3H_7OCH=CHPO(OCH_3)_2$. A mixture of 3.2 g of methyl alcohol, 7.9 g of dry pyridine, and 60 ml of dry benzene was introduced into a three-necked flask provided with stirrer, dropping funnel, and reflux condenser protected by a calcium chloride tube. With thorough cooling and stirring 10.15 g of 2-isopropoxyvinylphosphonic dichloride was added, and after the addition was complete the reaction mixture was heated for about one hour in a water bath. The precipitate was filtered off, and the filtrate was treated with saturated sodium carbonate solution and then dried with calcined sodium sulfate. Benzene was distilled off from a water bath, and the residue was vacuum-distilled. A second distillation yielded 6 g (62%) of a substance having b.p. 94-95° (2 mm); d_4^{20} 1.1042; n_D^{20} 1.4438

Found %: C 43.04; 42.96; H 8.09; 8.00
$C_7H_{15}O_4P$. Calculated %: C 43.29; H 7.73

The other diesters of 2-isoalkoxyvinylphosphonic acids were prepared by the method described above.

Diethyl 2-Isopropoxyvinylphosphonate $i\text{-}C_3H_7OCH=CHPO(OC_2H_5)_2$. Reaction between 4.6 g of absolute ethyl alcohol, 7.9 g of pyridine, and 10.15 g of 2-isopropoxyvinylphosphonic dichloride yielded 8.5 g of a substance having b.p. 103° (1 mm); d_4^{20} 1.0450; n_D^{20} 1.4428

Found %: C 48.50; 48.38; H 8.44; 8.24
$C_9H_{19}O_4P$. Calculated %: C 48.64; H 8.54

Dipropyl 2-Isopropoxyvinylphosphonate $i\text{-}C_3H_7OCH=CHPO(OC_3H_7\text{-}n)_2$. Reaction between 6 g of propyl alcohol, 7.9 g of dry pyridine, and 10.15 g of 2-isopropoxyvinylphosphonic dichloride yielded 9 g (72%) of a substance having b.p. 113° (1 mm); d_4^{20} 1.0141; n_D^{20} 1.4439

Found %: C 52.61; 52.78; H 9.37; 9.42
$C_{11}H_{23}O_4P$. Calculated %: C 52.80; H 9.92

Diisopropyl 2-Isopropoxyvinylphosphonate $i\text{-}C_3H_7OCH=CHPO(OC_3H_7\text{-}i)_2$. To a mixture of 6 g of isopropyl alcohol and 7.9 g of pyridine 10.15 g of 2-isopropoxyvinylphosphonic dichloride was added. Three successive fractionations yielded 7 g of an ester having b.p. 99° (2 mm); d_4^{20} 0.9973; n_D^{20} 1.4360

Found %: P 12.43; 12.37
$C_{11}H_{23}O_4P$. Calculated %: P 12.40

Dibutyl 2-Isopropoxyvinylphosphonate $i\text{-}C_3H_7OCH=CHPO(OC_4H_9\text{-}n)_2$. To a mixture of 7.4 g of butyl alcohol and 7.9 g of pyridine 10.15 g of 2-isopropoxyvinylphosphonic dichloride was added. Two successive fractionations yielded 9.3 g of ester having b.p. 132-133° (2 mm); d_4^{20} 0.9910; n_D^{20} 1.4460

Found %: C 55.77; 55.71; H 9.86; 10.01
$C_{13}H_{27}O_4P$. Calculated %: C 56.11; H 9.71

Diisobutyl 2-Isopropoxyvinylphosphonate $i\text{-}C_3H_7OCH=CHPO(OC_4H_9\text{-}i)_2$. To a mixture of 7.4 g of isobutyl alcohol and 7.9 g of pyridine 10.15 g of 2-isopropoxyvinylphosphonic dichloride was added. Three successive fractionations yielded 9 g of a substance having b.p. 116° (1 mm); d_4^{20} 0.9847; n_D^{20} 1.4440

Found %: C 56.21; 56.00; H 9.89; 9.86

$C_{13}H_{27}O_4P$. Calculated %: C 56.11; H 9.71

Diallyl 2-Isopropoxyvinylphosphonate $i\text{-}C_3H_7OCH = CHPO(OC_3H_5)_2$. To a mixture of 5.8 g of allyl alcohol and 8 g of pyridine 10.15 g of 2-isopropoxyvinylphosphonic dichloride was added. Three successive fractionations yielded 8 g (54%) of a substance having b.p. 120° (2 mm); d_4^{20} 1.0448; n_D^{20} 1.4651

Found %: C 53.88; 54.02; H 8.10; 7.95

$C_{11}H_{19}O_4P$. Calculated %: C 53.65; H 7.72

Dihexyl 2-Isopropoxyvinylphosphonate $i\text{-}C_3H_7OCH = CHPO(OC_6H_{13}\text{-}n)_2$. To a mixture of 21 g of hexyl alcohol and 7.9 g of pyridine 10.15 g 2-isopropoxyvinylphosphonic dichloride was added. Fractionation yielded 8.5 g of a substance having b.p. 149° (2 mm); d_4^{20} 0.9628; n_D^{20} 1.4498

Found %: C 61.17; 61.13; H 10.58; 10.58

$C_{17}H_{35}O_4P$. Calculated %: C 61.07; H 10.47

Bis(2-methoxyethyl) 2-Isopropoxyvinylphosphonate $i\text{-}C_3H_7OCH = CHPO(OCH_2 - CH_2OCH_3)_2$. Reaction of a mixture of 7.6 g of 2-methoxyethanol, 7.9 g of pyridine, and 10.15 g of 2-isopropoxyvinylphosphonic dichloride yielded 8 g (57%) of a substance having b.p. 155° (3 mm); d_4^{20} 1.1002; n_D^{20} 1.4555.

Found %: C 46.81; 46.91; H 8.11; 8.19

$C_{11}H_{23}O_6P$. Calculated %: C 46.80; H 8.15

Bis(2-ethoxyethyl) 2-Isopropoxyvinylphosphonate $i\text{-}C_3H_7OCH = CHPO(OCH_2 = CH_2OC_2H_5)_2$. To a mixture of 9 g of 2-ethoxyethanol, 7.9 g of pyridine, and 100 ml of benzene 10.15 g of 2-isopropoxyvinylphosphonic dichloride was added. Fractionation yielded 5 g of ester, b.p. 155° (1 mm); d_4^{20} 1.0652; n_D^{20} 1.4520

Found %: C 49.98; 50.10; H 8.78; 8.98

$C_{13}H_{27}O_6P$. Calculated %: C 50.32; H 8.70

Diesters of 2-Isobutoxyvinylphosphonic Acid

Dimethyl 2-Isobutoxyvinylphosphonate $i\text{-}C_4H_9OCH = CHPO(OCH_3)_2$. A solution of 3.2 g of methyl alcohol and 7.9 g of pyridine in 75 ml of benzene was prepared, and 10.85 g of 2-isobutoxyvinylphosphonic dichloride was added. The product isolated was 7.7 g (75%) of an ester having b.p. 105° (2 mm); d_4^{20} 1.0831; n_D^{20} 1.4487

Found %: C 46.24; 45.99; H 8.08; 8.09

$C_8H_{17}O_4P$. Calculated %: C 46.15; H 8.17

Methyl 2-isobutoxyvinylphosphonate is a colorless liquid, soluble in the usual organic solvents and in water.

Diethyl 2-Isobutoxyvinylphosphonate $i\text{-}C_4H_9OCH = CHPO(OC_2H_5)_2$. To a solution of 4.6 g of ethyl alcohol and 7.9 g of pyridine in 60 ml of benzene 10.85 g of 2-isobutoxyvinylphosphonic dichloride was added. At 110° (2 mm) 8.6 g (73%) of an ester came over; it had d_4^{20} 1.0310; n_D^{20} 1.4435

Found %: C 50.48; 50.26; H 8.67; 8.73

$C_{10}H_{21}O_4P$. Calculated %: C 50.84; H 8.89

Dipropyl 2-Isobutoxyvinylphosphonate $i\text{-}C_4H_9OCH = CHPO(OC_3H_7\text{-}n)_2$. To a mixture of 6 g of propyl alcohol, 7.9 g of pyridine, and 80 ml of benzene, 10.85 g of 2-isobutoxyvinylphosphonic dichloride was added. The product was 10.5 g of a substance having b.p. 124° (2 mm); d_4^{20} 1.0014; n_D^{20} 1.4442.

Found %: C 54.43; 54.45; H 9.34; 9.52

$C_{12}H_{25}O_4P$. Calculated %: C 54.54; H 9.46

Diisopropyl 2-Isobutoxyvinylphosphonate $i\text{-}C_4H_9OCH = CHPO(OC_3H_7\text{-}i)_2$. To a mixture of 6 g of isopropyl alcohol, 7.9 g of pyridine, and 80 ml of benzene, 10.85 g of 2-isobutoxyvinylphosphonic dichloride was added. Three successive vacuum distillations yielded 6.6 g of a substance having b.p. 110° (2 mm); d_4^{20} 0.9948; n_D^{20} 1.4405

Found %: C 54.62; 54.49; H 9.23; 9.31

$C_{12}H_{25}O_4P$. Calculated %: C 54.54; H 9.46

Dibutyl 2-Isobutoxyvinylphosphonate $i\text{-}C_4H_9OCH = CHPO(OC_4H_9\text{-}n)_2$. Reaction between 7.4 g of butyl alcohol, 7.9 g of pyridine, and 10.85 g of 2-isobutoxyvinylphosphonic dichloride yielded 10.4 g (70%) of a substance having b.p. 144° (1 mm); d_4^{20} 0.9849; n_D^{20} 1.4470

Found %: C 57.90; 57.92; H 10.32; 10.21
$C_{14}H_{29}O_4P$. Calculated %: C 57.53; H 9.93

Diisobutyl 2-Isobutoxyvinylphosphonate $i\text{-}C_4H_9OCH=CHPO(OC_4H_9\text{-}i)_2$. To a mixture of 7.4 g of isobutyl alcohol and 7.9 g of pyridine 10.85 g of 2-isobutoxyvinylphosphonic dichloride was added. The product isolated was 9.8 g of ester, b.p. 135° (2 mm); d_4^{20} 0.9804; n_D^{20} 1.4440

Found %: C 57.40; 57.32; H 9.97; 9.78
$C_{14}H_{29}O_4P$. Calculated %: C 57.53; H 9.93

Diallyl 2-Isobutoxyvinylphosphonate $i\text{-}C_4H_9OCH = CHPO(OCH_2-CH=CH_2)_2$. To a mixture of 5.8 g of allyl alcohol, 7.9 g of pyridine, and 60 ml of benzene 10.85 g of 2-isobutoxyvinylphosphonic dichloride was added. The product isolated was 9.5 g of ester, b.p. 130° (1 mm); d_4^{20} 1.0417; n_D^{20} 1.4643

Found %: C 55.58; 55.52; H 8.26; 8.08
$C_{12}H_{21}O_4P$. Calculated %: C 55.38; H 8.07

Dihexyl 2-Isobutoxyvinylphosphonate $i\text{-}C_4H_9OCH = CHPO(OC_6H_{13}\text{-}n)_2$. Reaction between 10.85 g of isobutoxyvinylphosphonic dichloride, 10.21 g of hexyl alcohol, and 7.9 g of pyridine yielded 10.5 g of a substance having b.p. 165° (1 mm); d_4^{20} 0.9597; n_D^{20} 1.4498

Found %: C 62.19; 61.97; H 10.84; 10.81
$C_{18}H_{37}O_4P$. Calculated %: C 62.06; H 10.63

Bis(2-methoxyethyl) 2-Isobutoxyvinylphosphonate $i\text{-}C_4H_9OCH = CHPO(OCH_2-CH_2OCH_3)_2$. To a mixture of 7.6 g of 2-methoxyethanol and 7.9 g of pyridine 10.85 g of isobutoxyvinylphosphonic dichloride was added. The product was 10.4 g of a substance having b.p. 163° (2 mm); d_4^{20} 1.0900; n_D^{20} 1.4543

Found %: C 48.45; 48.69; H 8.36; 8.36
$C_{12}H_{25}O_6P$. Calculated %: C 48.64; H 8.44

Bis(2-ethoxyethyl) 2-Isobutoxyvinylphosphonate $i\text{-}C_4H_9OCH = CHPO(OCH_2-CH_2OC_2H_5)_2$. To a mixture of 9 g of 2-ethoxyethanol, 7.9 g of pyridine, and 70 ml of benzene 10.85 g of isobutoxyvinylphosphonic dichloride was added. The product was 10.6 g of ester, b.p. 170° (2 mm); d_4^{20} 1.0533; n_D^{20} 1.4509

Found %: C 52.00; 51.88; H 8.87; 8.84
$C_{14}H_{24}O_6P$. Calculated %: C 51.85; H 8.95

Diesters of 2-Isopentyloxyvinylphosphonic Acid

Dimethyl 2-Isopentyloxyvinylphosphonate $(CH_3)_2CH-CH_2-CH_2-OCH=CHPO(OCH_3)_2$. To a mixture of 3.2 g of methyl alcohol, 7.9 g of pyridine, and 50 ml of benzene 11.55 g of 2-isopentyloxyvinylphosphonic dichloride was added. The product was 7 g of ester, b.p. 109.5° (1 mm); d_4^{20} 1.0667; n_D^{20} 1.4508

Found %: C 48.40; 48.54; H 8.72; 8.41
$C_9H_{19}O_4P$. Calculated %: C 48.64; H 8.55

Diethyl 2-Isopentyloxyvinylphsophonate $(CH_3)_2CH-CH_2-CH_2OCH=CHPO(OC_2H_5)_2$. To a mixture of 4.6 g of ethyl alcohol and 7.9 g of pyridine 11.55 g of 2-pentyloxyvinylphosphonic dichloride was added. The product was 8 g of a substance having b.p. 119° (1 mm); d_4^{20} 1.0928; n_D^{20} 1.4464

Found %: C 52.65; 52.58; H 9.21; 9.28
$C_{11}H_{23}O_4P$. Calculated %: C 52.80; H 9.20

Dipropyl 2-Isopentyloxyvinylphosphonate $(CH_3)_2CH-CH_2-CH_2OCH=CHPO(OC_3H_7\text{-}n)_2$. To a mixture of 6 g of propyl alcohol, 7.9 g of pyridine, and 75 ml of benzene 11.55 g of 2-isopentyloxyvinylphosphonic dichloride was added. The product was 8 g of a substance having b.p. 132° (1 mm); d_4^{20} 0.9960; n_D^{20} 1.4482

Found %: C 55.77; 55.68; H 9.73; 10.05
$C_{13}H_{27}O_4P$. Calculated %: C 56.11; H 9.71

Diisopropyl 2-Isopentyloxyvinylphosphonate $(CH_3)_2CHCH_2-CH_2OCH=CHPO(OC_3H_7\text{-}i)_2$. Reaction between 6 g of isopropyl alcohol, 7.9 g of pyridine, and 11.55 g of 2-isopentyloxyvinylphosphonic dichloride yielded 6 g of ester, b.p. 120° (2 mm); d_4^{20} 0.9866; n_D^{20} 1.4418

Found %: C 55.97; 56.19; H 9.64; 9.79
$C_{13}H_{27}O_4P$. Calculated %: C 56.11; H 9.71

Dibutyl 2-isopentyloxyvinylphosphonate $(CH_3)_2CH-CH_2-CH_2OCH=CHPO(OC_4H_9\text{-}n)_2$. A solution of 11.55 g of 2-isopentyloxyvinylphosphonic dichloride in 15 ml of dry benzene was added to a mixture of 7.4 g of butyl alcohol and 7.9 g of pyridine. The product was 7 g of an ester, b.p. 148° (1 mm); d_4^{20} 0.9896; n_D^{20} 1.4490

Found %: P 10.15; 9.97

$C_{15}H_{31}O_4P$. Calculated %: P 10.13

Diisobutyl 2-isopentyloxyvinylphosphonate $(CH_3)_2CH-CH_2-CH_2OCH=CHPO(OC_4H_9\text{-}i)_2$. To a mixture of 6.4 g of isobutyl alcohol, 6.83 g of pyridine, and 60 ml of benzene 10 g of 2-isopentyloxyvinylphosphonic dichloride was added. Two successive fractionations yielded 6.5 g of ester, b.p. 143° (2 mm); d_4^{20} 0.9734; n_D^{20} 1.4458

Found %: P 10.14; 10.14

$C_{15}H_{31}O_4P$. Calculated %: P 10.13

Diallyl 2-isopentyloxyvinylphosphonate $(CH_3)_2CH-CH_2-CH_2OCH=CHPO(OC_3H_5)_2$. Reaction between 5.2 g of allyl alcohol, 6.83 g of pyridine, and 10 g of 2-isopentyloxyvinylphosphonic dichloride yielded 6.7 g of a substance having b.p. 137° (1 mm); d_4^{20} 1.0335; n_D^{20} 1.4645

Found %: P 10.88; 11.11

$C_{13}H_{23}O_4P$. Calculated %: P 11.31

Dihexyl 2-isopentyloxyvinylphosphonate $(CH_3)_2CH-CH_2-CH_2OCH=CHPO(OC_6H_{13}\text{-}n)_2$. A solution of 10 g of 2-isopentyloxyvinylphosphonic dichloride in 15 ml of benzene was added to a mixture of 8.84 g of hexyl alcohol, 6.83 g of pyridine, and 75 ml of benzene. The product was 9.2 g of ester, b.p. 171° (1 mm); d_4^{20} 0.9618; n_D^{20} 1.4500

Found %: P 8.61; 8.33

$C_{19}H_{39}O_4P$. Calculated %: P 8.56

Bis(2-methoxyethyl) 2-isopentyloxyvinylphosphonate $(CH_3)_2CH-CH_2-CH_2OCH=CHPO(OCH_2-CH_2OCH_3)_2$. To a mixture of 6.5 g of 2-methoxyethanol and 6.83 g of pyridine 10 g of 2-isopentyloxyvinylphosphonic dichloride was added. Three successive vacuum distillations yielded 5.5 g of ester, b.p. 173° (1 mm); d_4^{20} 1.0758; n_D^{20} 1.4550

Found %: P 9.80; 10.00

$C_{13}H_{27}O_6P$. Calculated %: P 10.00

Bis(2-ethoxyethyl) 2-isopentyloxyvinylphosphonate $(CH_3)_2CH-CH_2-CH_2OCH=CHPO(OCH_2-CH_2OC_2H_5)_2$ To a mixture of 7.78 g of 2-ethoxyethanol, 6.83 g of pyridine, and 50 ml of benzene 10 g of 2-isopentyloxyvinylphosphonic dichloride was added. The product was 6 g of a substance having b.p. 179° (1 mm); d_4^{20} 1.0453; n_D^{20} 1.4527

Found %: C 53.22; 53.43; H 9.03; 9.17

$C_{15}H_{31}O_6P$. Calculated %: C 53.25; H 9.17

SUMMARY

The dimethyl, diethyl, dipropyl, diisopropyl, dibutyl, diisobutyl, diallyl, dihexyl, bis(2-methoxyethyl), and bis(2-ethoxyethyl) esters of 2-isopropoxy-, 2-isobutoxy-, and 2-isopentyloxy-vinylphosphonic acids have been prepared by the action of alcohols on 2-isopropoxy-, 2-isobutoxy-, and 2-isopentyloxy-vinylphosphonic dichlorides. The properties of the esters have been described.

LITERATURE CITED

[1] K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 2, 240. *

Received June 11, 1954

Institute of Heteroorganic Compounds
of the USSR Academy
of Sciences

---

* Consultant's Bureau Translation, p. 213.

BLANK
PAGE

DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 7. DIESTERS OF 2-PHENOXYVINYLPHOSPHONIC ACID

K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov

In continuation of our previous investigations on the synthesis of esters of 2-alkoxyvinylphosphonic acids by the action of alcohols on 2-alkoxyvinylphosphonic dichlorides in presence of pyridine [1] we have prepared esters of 2-phenoxyvinylphosphonic acid by analogous means. The esters obtained are colorless viscous liquids that can be vacuum-distilled without decomposition. They are all soluble in organic solvents, but are insoluble in water.

Some constants of the 2-phenoxyvinylphosphonic esters obtained are given in the table.

TABLE

Formula of substance	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}
$C_6H_5-O-CH=CHPO(OCH_3)_2$	128 (2)	1.5233	1.2871
$C_6H_5-O-CH=CHPO(OC_2H_5)_2$	140 (2)	1.5070	1.1367
$C_6H_5-O-CH=CHPO(OC_3H_7\text{-}n)_2$	147 (2)	1.4994	1.0934
$C_6H_5-O-CH=CHPO(OC_3H_7\text{-}i)_2$	135 (2)	1.4970	1.0870
$C_6H_5-O-CH=CHPO(OC_4H_9\text{-}n)_2$	165 (2)	1.4971	1.0648
$C_6H_5-O-CH=CHPO(OC_4H_9\text{-}i)_2$	157 (2)	1.4938	1.0596
$C_6H_5-O-CH=CHPO(OC_3H_5)_2$	153 (2)	1.5220	1.1330
$C_6H_5-O-CH=CHPO(OC_6H_{13}\text{-}n)_2$	204 (1)	1.4925	1.0237
$C_6H_5-O-CH=CHPO(O-CH_2-CH_2-O-CH_3)_2$	188 (2)	1.5070	1.1755
$C_6H_5-O-CH=CHPO(O-CH_2-CH_2-O-C_2H_5)_2$	198 (2)	1.5014	1.1386

The boiling points, refractive indices, and densities of 2-phenoxyvinylphosphonic esters are higher than those of the corresponding esters of 2-n-alkoxyvinylphosphonic acids.

EXPERIMENTAL

Dimethyl 2-Phenoxyvinylphosphonate $C_6H_5OCH=CHPO(OCH_3)_2$. A mixture of 3.2 g of methyl alcohol, 7.9 g of pyridine, and 50 ml of benzene was introduced into a three-necked flask fitted with stirrer, dropping funnel, and reflux condenser protected by a calcium chloride tube. The mixture was stirred and cooled with ice and salt while a mixture of 11.85 g of 2-phenoxyvinylphosphonic dichloride and 15 ml of benzene was added. Pyridine hydrochloride was filtered off, and the filtrate was washed with sodium carbonate solution and dried with calcined sodium sulfate. The solvent was distilled from a water bath, and the residue was vacuum-fractionated. Refractionation yielded 8 g of ester, b.p. 128° (2 mm); d_4^{20} 1.2871; n_D^{20} 1.5233.

Found %: P 13.39; 13.41

$C_{10}H_{13}O_4P$. Calculated %: P 13.59

All the other esters were synthesized by this method.

Diethyl 2-Phenoxyvinylphosphonate $C_6H_5OCH=CHPO(OC_2H_5)_2$. To a mixture of 4.6 g of ethyl alcohol and 7.9 g of pyridine 11.85 g of 2-phenoxyvinylphosphonic dichloride was added. Three successive fractionations yielded 10 g of a substance having b.p. 140° (2 mm); d_4^{20} 1.1367; n_D^{20} 1.5070

Found %: C 56.39; 56.43; H 6.63; 6.76

$C_{12}H_{17}O_4P$. Calculated %: C 56.25; H 6.64

Dipropyl 2-Phenoxyvinylphosphonate $C_6H_5OCH=CHPO(OC_3H_7\text{-}n)_2$. To a mixture of 6 g of propyl alcohol and 7.9 g of pyridine 11.85 g of 2-phenoxyvinylphosphonic dichloride was added. The product was 10 g of ester having b.p. 147° (2 mm); d_4^{20} 1.0934; n_D^{20} 1.4994

Found %: C 59.06; 58.91; H 7.65; 7.44

$C_{14}H_{21}O_4P$. Calculated %: C 59.15; H 7.39

Diisopropyl 2-Phenoxyvinylphosphonate $C_6H_5OCH = CHPO(OC_3H_7\text{-}i)_2$. To a mixture of 6 g of isopropyl alcohol, 7.9 g of pyridine, and 80 ml of benzene 11.85 g of 2-phenoxyvinylphosphonic dichloride was added. Three successive fractionations yielded 6 g of a substance having b.p. 135° (2 mm); d_4^{20} 1.0870; n_D^{20} 1.4970.

Found %: C 59.10; 59.33; H 7.31; 7.21

$C_{14}H_{21}O_4P$. Calculated %: C 59.15; H 7.39

Dibutyl 2-Phenoxyvinylphosphonate $C_6H_5OCH = CHPO(OC_4H_9\text{-}n)_2$. To a mixture of 7.4 g of butyl alcohol and 7.9 g of pyridine 11.85 g of 2-phenoxyvinylphosphonic dichloride was added. Two successive fractionations yielded 10.7 g of ester, b.p. 165° (2 mm); d_4^{20} 1.0648; n_D^{20} 1.4971

Found %: P 9.75; 9.77

$C_{16}H_{25}O_4P$. Calculated %: P 9.93

Diisobutyl 2-Phenoxyvinylphosphonate $C_6H_5OCH = CHPO(OC_4H_9\text{-}i)_2$. Reaction between 7.4 g of isobutyl alcohol, 7.9 g of pyridine, and 11.85 g of 2-phenoxyvinylphosphonic dichloride yielded 11 g of a substance having b.p. 157° (2 mm); d_4^{20} 1.0596; n_D^{20} 1.4938.

Found %: C 61.22; 61.21; H 7.90; 7.90

$C_{16}H_{25}O_4P$. Calculated %: C 61.53; H 8.01

Diallyl 2-Phenoxyvinylphosphonate $C_6H_5OCH = CHPO(OC_3H_5)_2$. To a mixture of 5.8 g of allyl alcohol and 7.9 g of pyridine 11.85 g of 2-phenoxyvinylphosphonic dichloride was added. Three successive fractionations yielded 5 g of ester, b.p. 153° (2 mm); d_4^{20} 1.1330; n_D^{20} 1.5220.

Found %: C 59.47; 59.60; H 6.15; 6.32

$C_{14}H_{17}O_4P$. Calculated %: C 60.00; H 6.07

Diallyl 2-phenoxyvinylphosphonate is a clear viscous liquid; it polymerizes when heated in presence of benzoyl peroxide.

Dihexyl 2-Phenoxyvinylphosphonate $C_6H_5OCH = CHPO(OC_6H_{13}\text{-}n)_2$. To a mixture of 10.21 g of hexyl alcohol, 7.9 g of pyridine, and 50 ml of benzene, 11.85 g of 2-phenoxyvinylphosphonic dichloride was added. The product was 10.8 g of a substance having b.p. 204° (1 mm); d_4^{20} 1.0237; n_D^{20} 1.4925

Found %: C 65.15; 65.25; H 8.80; 8.81

$C_{20}H_{33}O_4P$. Calculated %: C 65.21; H 8.94

Bis(2-methoxyethyl) 2-Phenoxyvinylphosphonate $C_6H_5OCH = CHPO(OCH_2 - CH_2OCH_3)_2$. A mixture of 7.6 g of 2-methoxyethanol and 7.9 g of pyridine was diluted with 70 ml of benzene, and 11.85 g of 2-phenoxyvinylphosphonic dichloride was added. The product was 11.2 g of ester, b.p. 188° (2mm); d_4^{20} 1.1755; n_D^{20} 1.5070

Found %: C 53.45; 53.27; H 6.48; 6.73

$C_{14}H_{21}O_6P$. Calculated %: C 53.16; H 6.64

Bis(2-ethoxyethyl) 2-Phenoxyvinylphosphonate $C_6H_5OCH = CHPO(OCH_2 - CH_2OC_2H_5)_2$. To a mixture of 9 g of 2-ethoxyethanol and 7.9 g of pyridine 11.85 g of 2-phenoxyvinylphosphonic dichloride was added. The product was 10 g of ester, b.p. 198° (2 mm); d_4^{20} 1.1386; n_D^{20} 1.5014

Found %: C 55.62; 55.64; H 7.30; 7.50

$C_{16}H_{25}O_6P$. Calculated %: C 55.81; H 7.26

SUMMARY

The dimethyl, diethyl, dipropyl, diisopropyl, dibutyl, diisobutyl, diallyl, dihexyl, bis(2-methoxyethyl), and bis(2-ethoxyethyl) esters of 2-phenoxyvinylphosphonic acid have been prepared by the action of 2-phenoxyvinylphosphonic dichloride on alcohols in presence of pyridine. The properties of these esters have been described.

LITERATURE CITED

[1] K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955 No. 2, 240. *(See Consultant's Bureau Translation, p. 213.

Received June 11, 1954

Institute of Heteroorganic Compounds of the USSR Academy of Sciences

ACTION OF SOME ALKOXY COMPOUNDS ON TRIALKOXY- AND DIALKOXYCHLORO-STIBINES

B. A. Arbuzov and O. D. Samoilova

Organoantimony compounds in which different alkoxy groups are attached to the same antimony atom are unknown. It appeared to us that the most promising method of synthesis of mixed alkoxystibines was the method of partial transesterification, since this method was the simplest and most convenient for antimonous esters [1]. The transesterification method, or alcoholysis, is applicable to carboxylic esters [2] and esters of some inorganic acids [3]. However, whereas the transesterification of esters of orthosilicic, orthotitanic, boric, and phosphorous acids requires the presence of an alkaline or acid catalyst, antimonous esters undergo transesterification when treated with alcohols in absence of catalyst.

The syntheses of mixed esters of antimonous acid were effected by partial transesterification of triethyl antimonite triethoxystibine with an equimolecular amount of a higher alcohol. For antimonous esters partial transesterification proceeds with simultaneous formation of three products, which result by the replacement of one, two, and three R radicals, respectively, by R', as indicated in the equation:

$$\mathrm{Sb(OR)_3 + R'OH} \begin{cases} \rightarrow \mathrm{Sb(OR)_2(OR') + ROH} \\ \rightarrow \mathrm{Sb(OR)(OR')_2 + 2ROH} \\ \rightarrow \mathrm{Sb(OR')_3 + 3ROH} \end{cases}$$

The unsymmetrical esters were separated in the first fractionation. It was found that the temperature of the oil bath must be carefully controlled, for redistillation and overheating cause disproportionation of the esters with formation of the symmetrical antimonous esters. Symmetrization occurs very readily when the mixed esters are heated for a short time: thus, when butoxydiethoxystibine was heated for the purpose of fractionation, triethyl and tributyl antimonites were isolated. The same phenomenon was observed in the course of the redistillation of ethoxybisisopentyloxystibine.

Butoxydiethoxy-, diethoxyisopentyloxy-, diethoxyhexyloxy-, dibutoxyethoxy-, ethoxybisisopentyloxy-, and ethoxybishexyloxy-stibines were prepared by the method of partial transesterification. These substances are colorless, fairly mobile liquids, which are very readily hydrolyzed when exposed to the atmosphere, so that it was difficult to measure their physical constants. The physical constants of the synthesized esters are given in the table.

Although the method of partial transesterification has been applied with success to the reaction of trialkyl and dialkyl hydrogen phosphites with higher alcohols, such as octyl, nonyl, and hexadecyl alcohols, we have not succeeded in preparing unsymmetrical antimonous esters having radicals higher than hexyl; only symmetrical esters were obtained.

TABLE

$\mathrm{Sb(OR)_n(OR')_{3-n}}$	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}
$\mathrm{Sb(OC_2H_5)_2(OC_4H_9\text{-}n)}$	109-110 (7)	1.4902	1.3990
$\mathrm{Sb(OC_2H_5)(OC_4H_9\text{-}n)_2}$	129-130 (7)	1.4861	1.3051
$\mathrm{Sb(OC_2H_5)_2(OC_5H_{11}\text{-}i)}$	120-121 (6)	1.4856	1.3452
$\mathrm{Sb(OC_2H_5)(OC_5H_{11}\text{-}i)_2}$	136-137 (3)	1.4815	1.2630
$\mathrm{Sb(OC_2H_5)_2(OC_6H_{13})}$	151-152 (4)	1.4840	1.3313
$\mathrm{Sb(OC_2H_5)(OC_6H_{13})_2}$	171-172 (4)	1.4743	1.1982

The transesterification of antimonous esters occurs not only with alcohols, but also with other alkoxy compounds. We found that, when triethoxystibine was treated with carboxylic esters, exchange occurred very readily between the alkoxy radicals of the two esters (at the boiling point of the carboxylic ester, in absence of catalyst):

$$\mathrm{Sb(OC_2H_5)_3 + 3ROOCCH_2R' \rightarrow Sb(OR)_3 + 3R'CH_2COOC_2H_5.}$$

We have studied the actions of butyl acetate, isopentyl acetate, and phenyl benzoate on triethoxystibine, and have obtained, respectively tributoxy-, trisisopentyloxy-, and triphenoxy-stibine. It should be noted that the higher the alkoxy radical of the carboxylic ester, the more complete the transesterification; transesterification by means of butyl acetate was found to be much more difficult than transesterification by means of isopentyl acetate.

The replacement of an alkoxy radical in an antimonous ester occurs also when the ester is treated with a carboxylic acid, when the corresponding alcohol is eliminated and a mixed anhydride of the carboxylic acid with the diester of antimonous acid is formed. Thus, reaction of acetic acid with triethoxystibine led to the synthesis of acetoxydiethoxystibine. This compound is thermally unstable: it decomposes at 100-105° with formation of ethyl acetate.

The ability to undergo transesterification under mild conditions is not confined to trialkoxystibines. Our experiments show that dialkoxychlorostibines are also able to react with higher alcohols with replacement of alkoxy groups; the chlorine is not affected. By the action of two molecular proportions of butyl alcohol on chlorodiethoxystibine, of isopentyl alcohol on chlorodiethoxystibine, and of hexyl alcohol on dibutoxychlorostibine, we synthesized dibutoxychlorostibine, chlorobisisopentyloxystibine, and chlorobishexyloxystibine, respectively. The reactions went smoothly and gave almost quantitative yields of the dialkoxychlorostibines having the longer radical; they are suitable as preparative methods.

EXPERIMENTAL

Reaction of Triethoxystibine with Butyl Alcohol. Equimolecular amounts of triethoxystibine (18 g) and butyl alcohol (4.5 g) were placed in an Arbuzov flask. The reaction mixture was heated at 110-115°, and 2.8 g of ethyl alcohol came over at 78-84° (the theoretical amount was 3.2 g). Fractionation of the reaction products yielded:

Frac. I, b.p. 87 – 89° (7 mm); 6.4 g
Frac. II, b.p. 89 – 109(7 mm); 0.8 g
Frac. III, b.p. 109–110° (7 mm); 4.9 g
Frac. IV, b.p. 110–129° (7 mm); 0.5 g
Frac. V b.p. 129–130° (7 mm); 3.2g
Frac. VI b.p. 130–140° (7 mm); 0.4 g
Frac. VII b.p. 140 – 141° (7 mm); 1.3g

The boiling point of Fraction I indicated that it was unchanged triethoxystibine. Fraction III b.p. 109-110° (7 mm); d_4^{20} 1.3990; n_D^{20} 1.4902, was butoxydiethoxystibine, a liquid that was readily hydrolyzed by the moisture of the air.

Found %: Sb 42.91; 42.55
$C_8H_{19}O_3Sb$. Calculated %: Sb 42.72

Fraction V, b.p. 129-130° (7 mm); d_4^{20} 1.3051; n_D^{20} 1.4861, was dibutoxyethoxystibine.

Found %: Sb 39.30
$C_{10}H_{23}O_3Sb$. Calculated %: Sb 38.94

The boiling point of Fraction VII indicated that it was tributoxystibine.

Effect of High Temperature on Butoxydiethoxystibine. Butoxydiethoxystibine (4.9 g) was heated at 150-160° for 20 minutes in an Arbuzov flask. Fractionation of the reaction products yielded:

Frac. I, b.p. 82- 83° (5 mm); 2.9 g
Frac. II, b.p. 136-137° (5 mm); 1.6 g

The boiling point of Fraction I indicated that it was triethoxystibine. Fraction II (b.p. 136-137°/ 5 mm) was tributoxystibine.

Reaction of Triethoxystibine with Isopentyl Alcohol. A mixture of 20 g of triethoxystibine and 6.8 g of isopentyl alcohol (obtained from fusel oil and boiling at 131-132°) was heated at 120-125°. Ethyl alcohol (2.9 g, the theoretical amount being 3.6 g) came over at 78-72°. Fractionation of the reaction product yielded:

Frac. I, b.p. 84-85° (6 mm); 3.2g
Frac. II, b.p. 85-119°(6 mm); 0.6g
Frac. III, b.p. 119-120°(6 mm); 4.5g
Frac. IV, b.p. 120-132°(3 mm); 0.9g
Frac. V, b.p. 132-133° (3 mm); 4.9g
Frac. VI, b.p. 133-150° (3 mm); 0.4 g
Frac. VII, b.p. 151-152° (3 mm); 7.2g

The boiling points of Fractions I and VII indicated that these fractions were triethoxy- and trisisopentyloxy-stibine, respectively. Fraction III, b.p. 120-121° (6 mm); d_4^{20} 1.3452; n_D^{20} 1.4856, was diethoxyisopentyloxystibine.

Found %: Sb 41.13; 41.17

$C_9H_{21}O_3Sb$. Calculated %: Sb 40.75

Fraction V, b.p. 136-137° (3 mm); d_4^{20} 1.2630; n_D^{20} 1.4815, was ethoxybisisopentyloxystibine.

Found %: Sb 35.77; 35.70

$C_{12}H_{27}O_3Sb$. Calculated %: Sb 35.73

Redistillation of Ethoxybisisopentyloxystibine. Vacuum distillation of 4.5 g of ethoxybisisopentyloxystibine from an Arbuzov flask yielded:

Frac. I. b.p. 84-85° (6 mm); 1.0g
Frac. II. b.p. 157-158° (6 mm); 2.7g,

The boiling points of the fractions indicated that the first was triethoxystibine and the second trisisopentyloxystibine.

Reaction of Triethoxystibine with Hexyl Alcohol. Equimolecular amounts of triethoxystibine (18 g) and hexyl alcohol (7.1 g) were heated together in an Arbuzov flask at 120-125°. Ethyl alcohol came over at 78-85° (2.0 g, the theoretical amount being 2.8 g). Fractionation of the reaction products yielded:

Frac. I. b.p. 85-105° (8 mm); 6.2g
Frac. II. b.p. 133-135° (4 mm); 2.3g
Frac. III. b.p. 135-170° (4 mm); 0.7g
Frac. IV. b.p. 170-173° (4 mm); 2.1g
Frac. V. b.p. 190-191° (4 mm); 4.6g

Fraction I was redistilled and boiled at 94-95° (10 mm), which corresponded to triethoxystibine. Fraction VI was trishexyloxystibine. Fraction II, b.p. 133-135° (4 mm); n_D^{20} 1.4840; d_4^{20} 1.3313, was diethoxyhexyloxystibine.

Found %: Sb 39.59; 39.12

$C_{10}H_{23}O_4Sb$. Calculated %: Sb 38.93

Fraction IV, b.p. 170-173° (4 mm); n_D^{20} 1.4743; d_4^{20} 1.1982, was ethoxybishexyloxystibine.

Found %: Sb 33.53; 33.39

$C_{14}H_{31}O_3Sb$. Calculated %: Sb 33.02

Reaction of Triethoxystibine with Butyl Acetate. A mixture of 4 g of triethoxystibine and 6 g of butyl acetate (b.p. 125-125.5°) was prepared in an Arbuzov flask. The mixture was heated at 100-110° for one hour, and a liquid very slowly distilled over (1 g; b.p. 77-85°); it was probably ethyl acetate. Fractionation of the reaction products yielded:

Frac. I. b.p. 124-126°; 3.2g
Frac. II. b.p. 95-96° (11 mm); 2.8 g
Frac. III. b.p. 139-141 (11 mm); 0.6 g

Fractions I and II were unchanged butyl acetate and unchanged triethoxystibine, respectively. The boiling point of Fraction III indicated that it was tributoxystibine.

Reaction of Triethoxystibine with Isopentyl Acetate. To 5 g of triethoxystibine 8 g of isopentyl acetate (b.p. 148-148.5°) was added. The mixture was heated at 110-115° for 45 minutes, and 4.8 g of a liquid came over at 78-87°. This liquid, which after redistillation had b.p. 78-79°; d_4^{20} 0.8906; n_D^{20} 1.3710, was ethyl acetate (the reported constants are b.p. 77.18°, d_4^{20} 0.92446 [4]. Fractionation of the reaction products yielded:

Frac. I b.p. 125-126°; 0.6 g
Frac. II b.p. 156-157° (6 mm); d_4^{20} 1.1885; 6.1g

The boiling point of Fraction II indicated that this fraction was trisisopentyloxystibine. It was obtained in 82.4 % yield.

Reaction of Triethoxystibine with Phenyl Benzoate. A mixture of 8 g of triethoxystibine and 18.6 g of phenyl benzoate was heated at 140-150° for 30 minutes. Fractionation of the reaction products yielded:

Frac. I b.p. 89-89.5° (10 mm); 12.8g
Frac. II. b.p. 238-242° (4 mm); 9.3 g

Fraction I, b.p. 89-89.5° (10 mm); d_4^{20} 1.0489; n_D^{20} 1.5064, was ethyl benzoate (the literature [5] gives b.p. 211.2°; d_4^{15} 1.0509; n_D^{15} 1.5079 [5]. The fraction boiling at 238-242° (4 mm) melted at 99-101°; it was difficult to distill. It was triphenoxystibine and was obtained in 77.4 % yield.

Found %: Sb 30.09; 30.30

$C_{18}H_{15}O_3Sb$. Calculated %: Sb 30.38

Reaction of Triethoxystibine with Glacial Acetic Acid. Glacial acetic acid (2.3 g) was added slowly to 10 g of triethoxystibine. Reaction proceeded with evolution of heat. After the whole of the glacial acetic acid had been added the reaction mixture crystallized; there was no odor of ethyl acetate. The mixture was warmed in a water bath (60-65°), and at a residual pressure of 90 mm 1.4 g of a liquid came over at 35-40°; after being redistilled it had b.p. 38-78.5; d_4^{20} 0.7916. According to its physical constants the liquid was ethyl alcohol, for which the literature [6] gives b.p. 78.3°, d_4^{20} 0.78945. The residue in the flask crystallized out. A small amount of this residue was quickly washed with ether on a sintered-glass filter and then dried in a vacuum desiccator. It melted at 50-51°.

Found %: CH_3COOH 21.68

$C_6H_{13}O_4Sb$ Calculated %: CH_3COOH 22.15

Found %: Sb 44.72

$C_6H_{13}O_4Sb$ Calculated %: Sb 44.96

The crystalline product (9 g) was heated, and when the temperature of the oil bath was 100-110° the substance decomposed with separation of a liquid (2.1 g), and a white powder remained in the flask. The liquid was distilled twice and then had b.p. 77-78°; d_4^{20} 0.8931. According to its physical constants this liquid was ethyl acetate, for which the literature [4] gives b.p. 77.18° and d_4^{20} 0.92446 [4].

Action of Butyl Alcohol on Chlorodiethoxystibine. A mixture of 12 g of chlorodiethoxystibine (b.p. 106°/10 mm) and 6.8 g of butyl alcohol was prepared in an Arbuzov flask and was then heated at 110-115°, when ethyl alcohol came over at 77-82° (3.9 g). A Beilstein test for chlorine was negative. Vacuum distillation gave 14.6 g (90.0%) of a fraction having b.p. 147-148° (10 mm); d_4^{20} 1.5066. According to its physical constants the compound was dibutoxychlorostibine [7].

Action of Isopentyl Alcohol on Chlorodiethoxystibine. A mixture of 10 g of chlorodiethoxystibine and 6.3 g of isopentyl alcohol was heated at 110-115°, and 3.1 g of ethyl alcohol came over at 77-82°. A Beilstein test for chlorine was negative. Vacuum distillation gave 12.0 g (89.5%) of a fraction having b.p. 140-141° (3 mm); d_4^{20} 1.3891. The substance was chlorobisisopentyloxystibine.

Found %: Sb 37.10; 37.11; Cl 10.62; 10.41

$C_{10}H_{22}O_2ClSb$. Calculated %: Sb 36.76; Cl 10.70

Action of Hexyl Alcohol on Dibutoxychlorostibine. A mixture of 13 g of dibutoxychlorostibine was heated with 8.7 g of hexyl alcohol, and butyl alcohol distilled over at a residual pressure of 90 mm. The butyl alcohol (5.5 g) was redistilled and then boiled at 115–117°. The residue was vacuum-distilled and yielded 12.1 g (79.1%) of a fraction boiling at 170–172° (3 mm). The boiling point of the fraction indicated it to be chlorobishexyloxystibine [7].

SUMMARY

1. Both full and partial esters of antimonous acid are able to undergo transesterification when treated with alcohols or carboxylic esters.

2. Carboxylic acids react with antimonous esters with formation of mixed anhydrides.

3. Eight antimonous esters that have not been described previously were synthesized.

4. Dialkoxychlorostibines can undergo transesterification with higher alcohols with formation of dialkoxychlorostibines containing higher alkyl radicals.

LITERATURE CITED

[1] B. A. Arbuzov and V. S. Vinogradova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1951 No. 5, 551.

[2] C. Friedel and R. Crafts, Ann. 133, 207 (1865).

[3] B. A. Arbuzov and T. G. Shavsha, Proc. Acad. Sci. USSR, 68, 259 (1949); B. A. Arbuzov and Z. G. Isaeva, J. Gen. Chem. 22, 566 (1952);* A. N. Nesmeyanov, R. Kh. Freidlina, and O. V. Nogina, Bull. Acad. Sci.

---

* Consultant's Bureau Translation, p 629 .

USSR, Div. Chem. Sci. 1951, No. 5, 518.

[4] S. Young, E. Forter, J. Chem. Soc. 83, 47 (1903)

[5] E. Linnemann, Ann. 160, 208 (1871); I. S. Lumsden, J. Chem. Soc. 87, 94 (1905).

[6] I. W. Winkler, Ber. 38, 3615, 1905; D. I. Mendeleev, Ann. Physik, 138, 103 (1869).

[7] B. A. Arbuzov and O. D. Samoilova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1951, No. 6, 717.

Received July 9, 1954

A. M. Butlerov Research Institute
V. I. Ulyanov-Lenin State University
Kazan

BLANK
PAGE

SYNTHESIS OF CHLORAMPHENICOL

G. Fodor, J. Toth, E. Kovacs, and J. Kiss

Among the numerous methods that have been developed for the synthesis of 2-amino-1-phenyl-1-propanol (norephedrine) and its derivatives containing substituents in the benzene ring, the most widely applied is that of Bruckner and his coworkers [1, 2], in which the starting material is an (alkoxypropenyl)benzene. Working by this method under Bruckner's direction, in 1943 I. Kovacs [3] prepared cinnamyl acetate (I), and she also prepared the acetic ester of 2-nitro-3-nitroso-3-phenyl-1-propanol (II), and from this, by treatment with acetic anhydride and sulfuric acid, the diacetic ester of 2-nitro-1-phenyl-1,3-propanediol (III). Electrolytic reduction of the last compound yielded 2-amino-1-phenyl-1,3-propanediol (IV) in the form of an N,O-diacetyl derivative.

The syntheses of compounds having structures similar to that of (IV) from halohydrins of cinnamyl alcohol had at that time been already reported in the literature [4, 5]. It was later shown, however, that these compounds were identical with 3-amino-3-phenyl-1,2-propanediol, a structural isomer of (IV) [6, 7].

Thus, the first synthesis of the compound (IV) was carried out at Szeged University. Later, this work acquired great importance, for the compound (IV) became one of the main intermediates in the synthesis of Chloromycetin (chloramphenicol) - an important antibiotic [6, 8].

In previous, stereochemical investigations we have studied, in particular, the configuration of 2-amino-1-phenyl-1-propanol (norephedrine), including the spatial disposition (conformation) of the hydroxyl and amino groups [9].

In 1949 we extended our investigations to chloramphenicol (VIIIa). The investigations took two directions: a study of the stereochemistry of this compound [10], and attempts to synthesize it.

We succeeded in converting DL-chloramphenicol into DL-N-benzoylnorpseudoephedrine without touching the asymmetric carbon atoms, and so proved its threo configuration, since Freudenberg and coworkers had shown that the configuration at the C atom carrying the amino group in (+)-pseudoephedrine is analogous to the configuration of L-(+)-alanine [11]. On the other hand, the configuration at the C atom carrying the hydroxyl group in (+)-pseudoephedrine is analogous to the configuration of mandelic acid [12], which was recently solved, successfully and finally, when the correlation between the configurations of (+)-mandelic and L-(+)-lactic acids was established [13]. Also, Vogler, who refers to the conversion of 3-phenylserine into (IV) [14], has proved the threo configuration of 3-phenylserine [15]. Diacetyl derivatives of the nitro compound (IX) and also diacetyl derivatives of the compound (IV) were found to behave like pseudoephedrine in the N to O acyl migration process, which indicates that the hydroxyl and amino groups in these compounds are sterically close [10]. Dunitz [16] has given an X-ray diffraction diagram for bromamphenicol, and this, according to Preobrazhensky [17], also proves the conformation referred to above. In our further discussion we therefore use projection formulas [10, 17], and these show not only the threo configuration of these compounds, but also the actual structures of their molecules.

Our investigations were carried out on optically inactive compounds, and in the further discussion each projection formula must be envisaged together with its mirror image.

The present paper gives an account of the synthetic investigations that we began in 1949. Our object was to repeat the preparation of the diacetyl derivative of (IV), as described in the above-mentioned paper by I. Kovacs [3], improve it from the preparative point of view, verify the stereochemical processes occurring, and, most important of all, investigate the conversion of the compound (IV) into chloramphenicol.

Compounds (II) and (IIIa) were obtained in high yield and in a sufficiently pure state [3]. Treatment of (II) with bis(dichloroacetic) anhydride yielded O^3-acetyl-O^1-(dichloroacetyl)-2-nitro-1-phenyl-1,3-propanediol (IIIb). Hydrolysis of (IIIa) with weak acids yielded the crystalline nitro diol (IIIc), which, in the form of the sodium salt of its aci form, has been described by Rebstock and coworkers [6]. Both (IIIa) and (IIIb) were reduced electrolytically in a strongly acid medium. The reduction of (IIIb), however, was accompanied by hydrogenolysis of the chlorine atoms of the dichloroacetyl group with formation of a diacetyl derivative of (IV), identical with that obtained by the reduction of (IIIa). It should be noted that for both compounds the yield in the reduction reaction is low, but we have succeeded in effecting satisfactory catalytic reduction of (IIIa) over palladium, both

---

[*] These Hungarian authors' names have been given their native spellings, as they are known in British and American journals. If transcribed from the Russian, they would be G. Fodor, I. Tot, E. Kovach, and I. Kish. Publisher.

at normal and at high pressures.

The diacetyl derivative of (IV) was found to be identical with the compound obtained from the reduction product of DL-threo-3-phenylserine, indicating that this substance, and therefore also the nitro diacetic ester (IIIa), has the same configuration. Taking into account the fact that the crystalline cinnamyl acetate (I) is the trans form [18b], like the stable forms of some natural ethers derived from propenylbenzene [18a], we may conclude that the exchange $NO \rightleftharpoons OCOCH_3$ is probably succeeded by a Walden inversion and that NO and NO_2 react at the double bond as in trans addition reactions. The mechanism of this process has not yet been investigated from the stereochemical point of view, but it is a fact that Bruckner's synthesis [1,2] leads to compounds of the threo-pseudoephedrine series [9b].

By the reductions of the aci form of the nitro compound (IIIc), Controulis and coworkers have prepared both threo and erythro racemates of (IV). This is understandable, since the liberation of the nitro diol from its salt can, with equal probability, yield either epimeric modification. However, in the course of the reduction of the crystalline stereochemical individual (IIIa), no such change can occur.

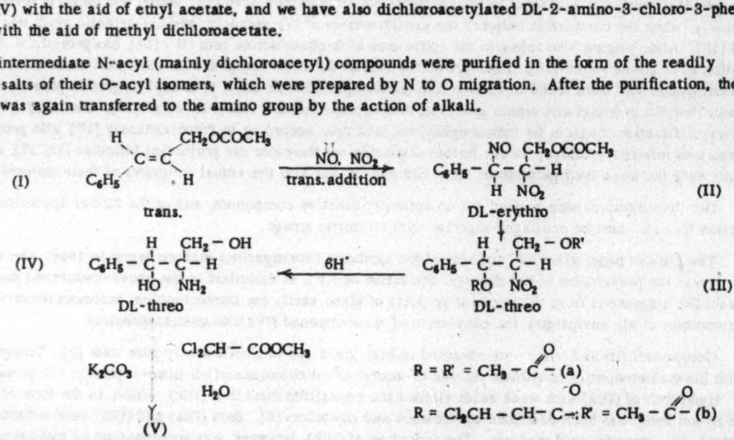
The conversion of the DL-threo amino diol (IV) into chloramphenicol had been effected prior to our work [6] as follows.

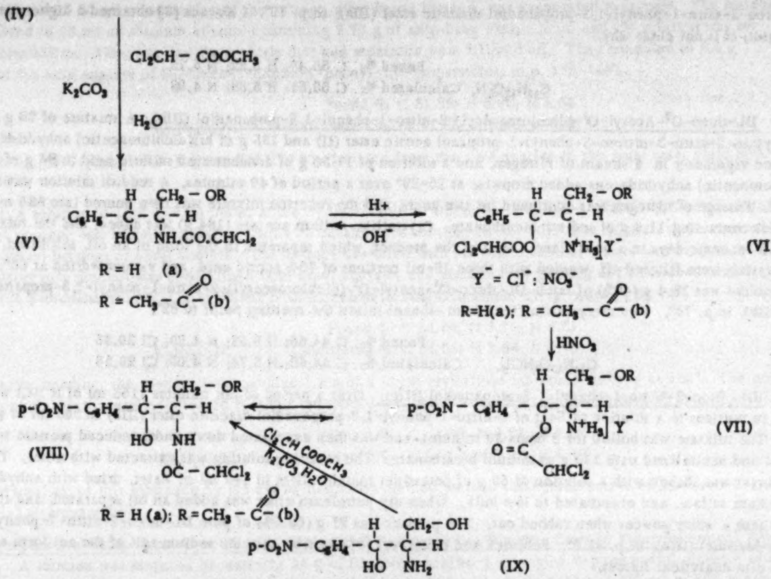
The triacetyl derivative of (IV) was nitrated, and the triacetyl derivative of (IX), which resulted, was deacetylated. A dichloroacetic acid residue was then introduced into the nitro amino diol (IX). We have found that the compound (IV) can be acylated, even in dilute aqueous solution, with methyl dichloroacetate, and we have isolated the previously undescribed DL-threo-2-(2,2-dichloroacetamido)-1-phenyl-1,3-propanediol (Va) in a crystalline state. It was found that this compound could be readily acylated on the primary hydroxyl group and that the resulting acetyl derivative (Vb) underwent a migration reaction in presence of acids, the acyl group then moving from the amino group to the secondary hydroxyl group.

In an alkaline medium this process proceeds in the reverse direction. During nitration, therefore, the two hydroxyl groups were protected with acyl groups, the amino group being protected by salt formation. The salt (VII) resulting from the nitration was converted by treatment with potassium carbonate into the O-acetylchloramphenicol (VIIIb), formed as a result of O to N acyl migration. When (VIIIb) was treated with caustic soda solution, it was converted immediately into (VIIIa), identical with DL-chloramphenicol. Nitration of the diacetic ester of (Va) (prepared by the complete acetylation of (Va), followed by deacetylation of the resulting diacetyl derivative of (VIIIa), yielded the same final product.

As far as we know, the acylation of amines of this type with the aid of carboxylic esters in aqueous alkaline solution has not been described previously. In order to verify the general applicability of this method, we have acetylated (IV) with the aid of ethyl acetate, and we have also dichloroacetylated DL-2-amino-3-chloro-3-phenyl-1-propanol with the aid of methyl dichloroacetate.

The intermediate N-acyl (mainly dichloroacetyl) compounds were purified in the form of the readily crystallizing salts of their O-acyl isomers, which were prepared by N to O migration. After the purification, the acyl residue was again transferred to the amino group by the action of alkali.





Thus, on the basis of a stereochemical study of chloramphenicol, and also of a study of N to O acyl migration in compounds of similar type, we have succeeded in effecting its synthesis in a simple, stereochemically elucidated sequence: (I) → (II) → (III) → diacetyl derivative of (IV) → (Va) → (Vb) → (VIb) → → (VII) → (VIIIa)

EXPERIMENTAL

Cinnamyl Acetate (I). This acetic ester was prepared by the method of Cherbuliez and coworkers [4] by the action of acetic anhydride on cinnamyl alcohol in presence of sodium acetate. At the end of the reaction the excess of acetic anhydride was distilled off under reduced pressure; with this modification cinnamyl acetate was obtained in 95% yield; b.p. 117° (2 mm).

DL-eruthro-2-Nitro-3-nitroso-3-phenyl-1-propanol Acetic Ester (II). A mixture of 400 g of sodium nitrite and 250 ml of water was stirred in a jar of dark glass, and a solution of 90 g of cinnamyl acetate in 450 ml of toluene was added. Then, at 0° over a period of seven hours, 1400 ml of 20% sulfuric acid was added dropwise, carbon dioxide being occasionally passed through the mixture to stop foaming. When addition of sulfuric acid was complete, the precipitate present in the toluene layer was filtered off and washed with cold water. The crystalline mass that separated on the filter was rubbed out with 100 ml of ethanol, drained, and washed again with 50 ml of ethanol and 100 ml of ether free from peroxides. The product was 89 g (69%) of white DL-erythro-2-nitro-3-nitroso-3-phenyl-1-propanol acetic ester (II), m.p. 124°. I. Kovacs [3] gave m.p. 117°. After standing for some weeks the substance became colored as a result of decomposition.

Found %: C 52.66; H 4.96; N 10.85
$C_{11}H_{12}O_5N_2$. Calculated %: C 52.38; H 4.80; N 11.11

DL-threo-2-Nitro-1-phenyl-1,3-propanediol Diacetic Ester (IIIa). The nitroso nitro compound (II) (56 g) was mixed with 224 g of acetic anhydride and, at 25-29° with rapid agitation in a stream of carbon dioxide, a mixture of 24 g of concentrated sulfuric acid and 72 ml of acetic anhydride was added dropwise over a period of 40 minutes. Further stirring in a stream of carbon dioxide resulted in the formation of a light-yellow solution after about 50 minutes. The solution was filtered and poured into 1000 ml of ice water; stirring was continued for three hours. After the mixture had stood in a cold place for 3-4 days, the oil that separated crystallized. It was filtered off and dried; the yield was 43 g (69%). Recrystallization from ethanol or 75% acetic acid yielded

DL-threo-2-nitro-1-phenyl-1,3-propanediol diacetic ester (IIIa), m.p. 72°. I. Kovacs [3] obtained a higher melting point; it is not clear why.

Found %: C 55.40; H 5.22; N 5.12
$C_{13}H_{15}O_6N$. Calculated %: C 55.51; H 5.38; N 4.98

DL-threo-O^3-Acetyl-O^1-(dichloroacetyl)-2-nitro-1-phenyl-1,3-propanediol (IIIb). A mixture of 29 g of DL-erythro-2-nitro-3-nitroso-3-phenyl-1-propanol acetic ester (II) and 135 g of bis(dichloroacetic) anhydride was agitated vigorously in a stream of nitrogen, and a solution of 11.55 g of concentrated sulfuric acid in 24 g of bis-(dichloroacetic) anhydride was added dropwise at 25-29° over a period of 40 minutes. A reddish solution was obtained. Passage of nitrogen was continued for two hours, and the reaction mixture was then poured into 885 ml of water containing 11.9 g of sodium bicarbonate. Crystalline sodium acetate (184 g) was added, and the mixture was left for some days in a cold place. Most of the product, which separated in the form of an oil, solidified. The crystals were filtered off, washed with three 16-ml portions of 75% acetic acid, and vacuum-dried at 60°. The product was 18.4 g (46%) of crude DL-threo-O^3-acetyl-O^1-(dichloroacetyl)-2-nitro-1-phenyl-1,3-propanediol (IIIb), m.p. 74°. Two recrystallizations from ethanol raised the melting point to 82°.

Found %: C 44.65; H 3.58; N 4.20; Cl 20.35
$C_{13}H_{13}O_6NCl_2$. Calculated %: C 44.46; H 3.74; N 4.00; Cl 20.25

DL-threo-2-Nitro-1-phenyl-1,3-propanediol (IIIc). Over a period of ten minutes 1156 ml of N HCl was added in portions to a solution of 54 g of 2-nitro-1-phenyl-1,3-propanediol diacetic ester (IIIa) in 960 ml of acetone. The mixture was boiled for 3 hours 30 minutes, and was then evaporated down under reduced pressure to 600 ml and neutralized with 130 g of sodium bicarbonate. The resulting solution was extracted with ether. The ether layer was shaken with a solution of 30 g of potassium metabisulfite in 140 ml of water, dried with anhydrous magnesium sulfate, and evaporated to low bulk. When dry petroleum ether was added an oil separated, and this turned into a white powder when rubbed out. The product was 27 g (68.5%) of pure DL-threo-2-nitro-1-phenyl-1,3-propanediol (IIIc), m.p. 82.5°. Rebstock and coworkers [6] describe only the sodium salt of the aci form and do not cite analytical figures.

Found %: C 54.52; H 5.96; N 7.02
$C_9H_{11}O_4N$. Calculated %: C 54.82; H 5.62; N 7.10

DL-threo-O^3-Acetyl-2-acetamido-1-phenyl-1,3-propanediol. 2-Nitro-1-phenyl-1,3-propanediol diacetic ester (28 g) was dissolved in 8 ml of glacial acetic acid and hydrogenated in presence of 5 g of palladium supported on bone charcoal (Pd content about 12%) at a pressure of 40 atm. After three hours the catalyst was filtered off and the solution was evaporated down at low temperature and under reduced pressure. The residue was recrystallized from 50 ml of anhydrous ethyl acetate. The product was 10 g (40%) of DL-threo-O^3-acetyl-2-acetamido-1-phenyl-1,3-propanediol, m.p. 168-169°. I. Kovacs gives m.p. 158°. U. S. Patent 2483885 (Example 68) gives m.p. 167-168°.

Found %: C 62.03; H 6.75; N 5.46
$C_{13}H_{17}O_4N$. Calculated %: C 62.14; H 6.82; N 5.57

DL-threo-2-Acetamido-1-phenyl-1,3-propanediol Diacetic Ester. DL-threo-O^3-Acetyl-2-acetamido-1-phenyl-1,3-propanediol (1 g) was stirred with 5 ml of quinoline, and 1.5 g of acetic anhydride was added. The reaction mixture was set aside for 24 hours and then evaporated down under reduced pressure. The oily residue was crystallized from methanol, and yielded 1.1 g (90%) of pure DL-threo-2-acetamido-1-phenyl-1,3-propanediol diacetic ester, m.p. 79-80°. U. S. Patent 2483885 (Example 68) gives m.p. 79°.

DL-threo-2-Amino-1-phenyl-1,3-propanediol (IV). a) DL-threo-O^3-Acetyl-2-acetamido-1-phenyl-1,3-propanediol (25.12 g, i.e. 0.1 mole) was boiled with 5% hydrochloric acid for two hours, and the mixture was then evaporated to dryness under reduced pressure. The residue was crystallized from a 1 : 1 mixture of absolute ethanol and absolute ether, and yielded 16.8 g (82%) of the hydrochloride of DL-threo-2-amino-1-phenyl-1,3-propanediol, m.p. 192°. It is evident that the substance of m.p. 178° described in U. S. Patent 2513346, Example 2d, was insufficiently pure.

Found %: C 53.24; H 6.85; N 6.64; Cl 17.50
$C_9H_{14}O_2NCl$. Calculated %: C 53.07; H 6.93; N 6.88; Cl 17.41

b) DL-threo-2-Nitro-1-phenyl-1,3-propanediol diacetic ester (IIIa) (12.2 g), in 135 ml of anhydrous acetic acid containing 2.75 g of anhydrous oxalic acid, was hydrogenated at atmospheric pressure in presence of 2.5 g of palladium supported on bone charcoal (Pd content about 12%). When 3300 ml of hydrogen had been absorbed, the catalyst was filtered off and the solution was evaporated to dryness under reduced pressure. The residue was extracted with 50 ml of ethanol, and the extract, after being filtered, was evaporated to dryness. The residue was dissolved in 30 ml of absolute ethanol containing 2.75 g of anhydrous oxalic acid, and the solution was set aside to crystallize. After one day the crystals that had separated were filtered off. They consisted of 6.4 g (59.5%) of the acid oxalate of DL-threo-2-amino-1-phenyl-1,3-propanediol, m.p. 139-140°.

Found %: C 51.22; H 5.98; N 5.64

$C_{11}H_{15}O_6N$. Calculated %: C 51.36; H 5.88; N 5.45

2-Amino-1-phenyl-1,3-propanediol (IV) was isolated from the acid oxalate in the usual way: yield 85%; m.p. 82-83°.

c) A solution of 10.2 g (0.05 mole) of the hydrochloride of DL-threo-2-amino-1-phenyl-1,3-propanediol in 100 ml of water was rendered alkaline with 40% caustic soda solution (to pH 10). The solution was extracted with six 50-ml portions of ethyl acetate. The extract was dried with anhydrous sodium sulfate and evaporated down. The resulting oily product was crystallized from ethyl acetate, and yielded 5.85 g (70%) of DL-threo-2-amino-1-phenyl-1,3-propanediol (IV), m.p. 82-83°. U. S. Patent 2514376, Example 27, gives m.p. 81-83°.

Found %: C 64.64; H 7.75; N 8.21

$C_9H_{13}O_2N$. Calculated %: C 64.65; H 7.84; N 8.38

After standing, the mother liquor yielded 1.1 g of a white crystalline substance melting at 135°. The melting point and analytic results indicated that this compound was DL-threo-2-acetamido-1-phenyl-1,3-propanediol.

Found %: C 63.38; H 6.94; N 6.96

$C_{11}H_{15}O_3N$. Calculated %: C 63.14; H 7.23; N 6.70

Hydrolysis of this substance by the above-described method yielded the hydrochloride of DL-threo-2-amino-1-phenyl-1,3-propanediol.

Preparation of DL-threo-2-Acetamido-1-phenyl-1,3-propanediol Diacetic Ester by Electrochemical Reduction. A solution was prepared by warming 14 g of DL-threo-2-nitro-1-phenyl-1,3-propanediol diacetic ester (recrystallized from 60% acetic acid) with a mixture of 100 ml of glacial acetic acid and 200 ml of 96% ethanol. The solution was cooled to room temperature and poured into a one-liter beaker containing mercury to the depth of 1 cm. The mercury had been given a preliminary wash with nitric acid. A 20% solution of nitric acid was used as anode liquor. The anode liquor was contained in a porous cylinder fixed in the beaker, and it was necessary that its level should be the same as that of the solution of the substance to be reduced. The cathode liquor was acidified with 8 ml of fuming hydrochloric acid, and reduction was effected at a current density of 0.07 amp/sq. cm at 44-45°. The desired temperature was maintained by ice cooling. After two hours the yellow color of the reaction mixture disappeared, and the end of the reaction (about three hours) was indicated by a vigorous evolution of hydrogen. The reaction mixture was neutralized with sodium acetate and was evaporated at 35-40° under reduced pressure to a volume of 80-100 ml. Solid sodium bicarbonate was added to the residue with constant stirring until evolution of carbon dioxide ceased.

The mixture was extracted with three 100-ml portions of chloroform, and the extract was dried with sodium sulfate and evaporated under reduced pressure until it attained the consistency of a sirup. The red oil so obtained was dissolved in acetic acid, treated with bone charcoal, and set aside for 24 hours in a refrigerator. The white crystalline powder that separated was filtered off and washed on the filter with 3 ml of ice-cooled ethyl acetate. The yield of DL-threo-O^3-acetyl-2-acetamido-1-phenyl-1,3-propanediol [a diacetyl derivative of the compound (IV)] was 2.4 g. It melted at 162-164°, and after two recrystallizations from ethyl acetate its melting point was raised to 169-170°.

Electrochemical Reduction of DL-threo-O^3-Acetyl-O^1-(dichloroacetyl)-2-nitro-1-phenyl-1,3-propanediol (IIIb). The reduction was carried out in the apparatus described in the account of the preceding experiment. DL-threo-O^3-Acetyl-O^1-(dichloroacetyl)-2-nitro-1-phenyl-1,3-propanediol (3.5 g) was suspended in 40 ml of alcohol, and 2.5 ml of hydrochloric acid was added. Reduction was effected at a current density of 0.07 amp/sq. cm at 35-37°. The charge passed through the system was about 2.5 times the theoretical value. After the reduction treatment the mixture was stirred while 5 g of sodium bicarbonate was added. The reaction mixture was filtered and dried over sodium sulfate. The solution was evaporated to dryness under reduced pressure, and the resulting crystalline mass was extracted with hot ethyl acetate. The extract was evaporated under reduced pressure, and the crystalline substance obtained was recrystallized from ethyl acetate. The product was 0.7 g (28%) of a substance melting at 168°. A qualitative test for chlorine was negative.

Found %: C 61.90; H 6.87

$C_{13}H_{17}O_4$. Calculated %: C 62.14; H 6.82

Acylation of DL-threo-2-Amino-1-phenyl-1,3-propanediol with Esters in Aqueous Alkaline Medium. a) Ethyl acetate (200 ml) was added to a solution of 16.7 g (0.1 mole) of 2-amino-1-phenyl-1,3-propanediol (IV) in 100 ml of water. The solution was stirred vigorously, and 30 ml of a 40% caustic soda solution was added dropwise at 30° over a period of 50 minutes, care being taken that the pH of the solution remained in the range 6-8. The water phase was separated and extracted five times with 50-ml portions of ethyl acetate. The combined ethyl acetate solution was dried over anhydrous sodium sulfate, filtered, and evaporated down. The glassy residue was dissolved in 50 ml of absolute ethanol, the solution was cooled with ice, and a two-fold excess of a solution of HCl in absolute ethanol was added. The crystals that came down were filtered off and washed with a small amount of absolute ethanol. The product was 12.4 g (50.5%) of the hydrochloride of DL-threo-O^3-acetyl-2-amino-1-phenyl-1,3-propanediol, m.p. 178°.

The salt so obtained (12.4 g) was dissolved in 40 ml of water, and 6.0 g of anhydrous potassium carbonate was added at 20°. After ten minutes the mixture was extracted ten times with 50-ml portions of ethyl acetate. Treatment of the extract yielded an oil, which was crystallized from ethyl acetate and yielded 8.5 g (41%) of pure DL-threo-2-acetamido-1-phenyl-1,3-propanediol, m.p. 136-138°. The substance showed no melting point depression in admixture with a sample prepared by another method [6, 8].

b) Methyl dichloroacetate (71.5 g, i.e. 0.5 mole) was added to a solution of 20.4 g (0.1 mole) of the hydrochloride of 2-amino-1-phenyl-1,3-propanediol (IV). The mixture was stirred vigorously for about one hour, and at 6-8° 30 ml (0.3 mole) of 40% caustic soda solution was added dropwise in such a way that the pH of the solution remained in the range 6-8 throughout the reaction. The aqueous phase was separated and extracted six times with 50-ml portions of ethyl acetate. The combined extract was dried over anhydrous sodium sulfate and filtered. The solvents were removed, and the oil remaining was dissolved in 50 ml of absolute ethanol. A solution of 30 ml (0.3 mole) of HCl in absolute ethanol was then added. The crystals that separated (m.p. 190°) were filtered off and washed with 200 ml of a 1 : 1 ethanol-ether mixture. The product was 20.4 g (64.8%) of pure hydrochloride of DL-threo-O^1-(dichloroacetyl)-2-amino-1-phenyl-1,3-propanediol (VIa), m.p. 195°.

Found %: C 42.14; H 4.79; N 4.44; Cl 11.75; 33.83
$C_{11}H_{14}O_3NCl_3$. Calculated %: C 41.99; H 4.49 N 4.45 Cl 11.27; 33.81

DL-threo-2-(2,2-Dichloroacetamido)-1-phenyl-1,3-propanediol(Va). Ethyl acetate (90 ml) was added to a solution of 15.75 g (0.05 mole) of the hydrochloride of O^1-(dichloroacetyl)-2-amino-1-phenyl-1,3-propanediol (VIa) in 45 ml of water. The mixture was stirred at 25°, and 3.45 g (0.025 mole) of anhydrous potassium carbonate was added in small portions over a period of five minutes. The mixture was stirred for five minutes, and the aqueous layer was then separated and extracted four times with 25-ml portions of ethyl acetate. The extract was dried and evaporated, when 13.2 g of a light-yellow oil was obtained which solidified after some hours (yield 95%). Recrystallization from 50% aqueous ethanol yielded 11.8 g (78%) of DL-threo-2-(2,2-dichloroacetamido)-1-phenyl-1,3-propanediol (Va), m.p. 90°. After two further recrystallizations the melting point rose to 94-95°.

Found %: C 47.68; H 4.79; N 5.37; Cl total 25.05
$C_{11}H_{13}O_3Cl_2$. Calculated %: C 47.50; H 4.71; N 5.04; Cl total 25.50

DL-threo-2-(2,2-Dichloroacetamido)-1-phenyl-1,3-propanediol Diacetic Ester. A mixture of 11.19 g (0.04 mole) of DL-threo-2-(2,2-dichloroacetamido)-1-phenyl-1,3-propanediol (Va), 10 ml of anhydrous pyridine, and 12 ml of acetic anhydride was heated at 100° for 30 minutes and then evaporated down under reduced pressure. After a few days the reddish-yellow oily residue solidified. Crystallization of the residue from 20 ml of 60% ethanol yielded 12.2 g (83%) of crystalline DL-threo-2-(2,2-dichloroacetamido)-1-phenyl-1,3-propanediol. m.p. 93-95°.

Found %: C 49.91; H 4.52; N 3.87; Cl 19.65
$C_{15}H_{17}O_5NCl_2$. Calculated %: C 49.74; H 4.73; N 3.87; Cl 19.58

U. S. Patent 2538766 (Example 2b) refers to this compound, but no yield and no physical constants are given.

DL-threo-O^3-Acetyl-2-(2,2-dichloroacetamido)-1-phenyl-1,3-propanediol (Vb). Acetic anhydride (8 ml) was added to 5.56 g (0.02 mole) of DL-threo-2-(2,2-dichloroacetamido)-1-phenyl-1,3-propanediol (Va), and the mixture was maintained at 70° for 15 minutes. The slightly yellowish oil that remained after removal of acetic anhydride by distillation solidified after 24 hours (6.3 g). This substance was dissolved in 24 ml of ethyl acetate and crystallization was promoted by addition of 36 ml of petroleum ether. The product was 4.6 g (72%) of DL-threo-O^3-acetyl-2-(2,2-dichloroacetamido)-1-phenyl-1,3-propanediol (Vb), m.p. 97-99°, raised by recrystallization to 100-101°.

Found %: C 48.67; H 4.68; N 4.41; Cl 21.89
$C_{13}H_{15}O_4NCl_2$. Calculated %: C 48.76; H 4.72; N 4.37; Cl 22.18

Hydrochloride of DL-threo-O^3-Acetyl-O^1-(dichloroacetyl)-2-amino-1-phenyl-1,3-propanediol (VIb). To an ice-cooled solution of 3.2 g (0.01 mole) of DL-threo-O^3-acetyl-2-(2,2-dichloroacetamido)-1-phenyl-1,3-propanediol in 10 ml of absolute ether, 3.2 ml of a solution of HCl (0.02 mole) in absolute ethanol was added, and the mixture was set aside at 0°. On the next day the crystals that had formed were centrifuged off and washed three times with 3-ml portions of a 1 : 20 mixture of absolute ethanol and absolute ether. The product was 2.6 g (74%) of the hydrochloride of DL-threo-O^3-acetyl-O^1-(dichloroacetyl)-2-amino-1-phenyl-1,3-propanediol (VIb), m.p. 169-172°, raised to 187° by recrystallization from a 1 : 2 mixture of absolute ethanol and absolute ether.

Found %: C 43.52; H 4.75; N 4.23; Cl 30.18; 9.93
$C_{13}H_{16}O_4NCl_3$. Calculated %: C 43.78; H 4.52; N 3.93; Cl 29.83; 9.95

Nitrate of DL-threo-O^3-Acetyl-O^1-(dichloroacetyl)-2-amino-1-phenyl-1,3-propanediol (VIb). A solution of 0.94 g (0.015 mole) of nitric acid in 5 ml of dioxane was added to an ice-cooled solution of 3.2 g (0.01 mole) of O^3-acetyl-2-(2,2-dichloroacetamido)-1-phenyl-1,3-propanediol (Vb) in 10 ml of dioxane. The reaction mixture was set aside for some days at 0°, and a white microcrystalline substance separated, which was filtered off and washed with absolute ether. The product was 2.9 g (75.5%) of the nitrate of DL-threo-O^3-acetyl-O^1-(dichloroacetyl)-2-amino-1-phenyl-1,3-propanediol (VIb), m.p. 122-124°. Recrystallization from 12 ml of absolute ethanol yielded the pure substance, which melted at 126-128°.

Found %: C 41.08; H 4.38; N 7.22; Cl 18.87
$C_{13}H_{16}O_7N_2Cl_2$. Calculated %: C 40.75; H 4.21; N 7.31; Cl 18.51

Hydrochloride of DL-erythro-2-Amino-3-chloro-3-phenyl-1-propanol. 2-Acetamido-3-hydroxypropiophenone isolated from the racemic mixture remaining after the preparation of DL-threo-O^3-acetyl-2-acetamido-1-phenyl-1,3-propanediol was reduced and yielded a crystalline substance melting at 90-95°. This substance (30 g) was added to 90 ml of thionyl chloride, the mixture being cooled with ice. The mixture was allowed to stand for 15 minutes at room temperature, and 90 ml of water was then added dropwise. It was then heated for two hours at 100°, cooled, and set aside for 12 hours at − 20°. A white crystalline substance (14.6 g) separated. Recrystallization from a small amount of water yielded 11.8 g (28.2%) of the hydrochloride of 2-amino-3-chloro-3-phenyl-1-propanol, m.p. 187-188°.

Found %: C 48.96; H 5.95; N 6.41; Cl total 31.93; 16.19
$C_9H_{13}ONCl_2$. Calculated %: C 48.66; H 5.90; N 6.31; Cl total 31.93; 15.97

The mother liquor was evaporated down, and the residue was crystallized from a 1 : 1 mixture of absolute ethanol and absolute ether, when the hydrochloride of DL-threo-2-amino-1-phenyl-1,3-propanediol (IV), m.p. 192°, was obtained. The melting point of 178° that is given in U. S. Patent 2513346 (Example 2d) probably corresponds to a mixture of two substances indicated above.

DL-erythro-3-Chloro-2-(2,2-dichloroacetoamido)-3-phenyl-1-propanol. Methyl dichloroacetate (11 ml, i.e. 14.3 g) was added to a solution of 4.4 g (0.02 mole) of the hydrochloride of 2-amino-3-chloro-3-phenyl-1-propanol. The mixture was stirred vigorously at 8-10°, and over a period of about 30 minutes 6 ml of 40% caustic soda solution was added dropwise in such a way that the pH of the solution remained between 6 and 8. The layers were separated, and the aqueous layer was extracted five times with 50-ml portions of ethyl acetate. The combined extract was dried with anhydrous sodium sulfate and evaporated under reduced pressure. The oily residue was dissolved in 15 ml of ethyl acetate, the resulting solution was treated with bone charcoal, and crystallization was effected by addition of 60 ml of absolute ether, when 4.35 g (69%) of DL-erythro-3-chloro-2-(2,2-dichloroacetamido)-3-phenyl-1-propanol monohydrate, m.p. 147°, was obtained.

Found %: C 41.91; H 4.61; N 4.56; Cl 33.78
$C_{11}H_{12}O_2NCl_3 \cdot H_2O$. Calculated %: C 41.99; H 4.49; N 4.45; Cl 33.81

N to O Migration of the Acyl Residue. DL-erythro-3-Chloro-2-(2,2-dichloroacetamido)-3-phenyl-1-propanol monohydrate (0.28 g, i.e. 0.00112 mole) was dissolved in 5 ml of absolute ethanol, and, under ice-cooling, 0.34 ml of a 32.18% solution of HCl in absolute ethanol (0.00336 mole) was added. After a few minutes 0.22 g of white crystals of the hydrochloride of 2-amino-3-chloro-3-phenyl-1-propanol dichloroacetic ester, m.p. 194°, were precipitated.

Found %: C 39.52; H 4.12; N 4.30; Cl total 42.18
$C_{11}H_{13}O_2NCl_4$. Calculated %: C 39.67; H 3.93; N 4.21; Cl total 42.58

Found %: Cl^- 10.72
Calculated %: Cl^- 10.64

DL-threo-2-(2,2-Dichloroacetamido)-1-p-nitrophenyl-1,3-propanediol Diacetic Ester. 2-(2,2-Dichloroacetamido)-1-phenyl-1,3-propanediol diacetic ester (7.24 g, i.e. 0.02 mole) was dissolved in 20 ml of absolute chloroform, and this solution was added dropwise over a period of 50 minutes, with rapid stirring and cooling to 0°, to a mixture of 10 ml (18.2 g) of concentrated sulfuric acid and 1.45 ml (2.02 g; 0.022 mole) of nitric acid. The reaction mixture was stirred for 30 minutes and then poured in a thin stream onto 45 g of ice. The layers were separated, and the aqueous layer was extracted with four 8-ml portions of chloroform. The combined chloroform extract was shaken with two 6-ml portions of 10% sodium bicarbonate solution and with 5 ml of water. The chloroform solution was dried over anhydrous sodium sulfate and evaporated to dryness under reduced pressure. Recrystallization from 80% ethanol yielded 3.5 g (43%) of DL-threo-2-(2,2-dichloroacetamido)-1-p-nitrophenyl-1,3-propanediol diacetic ester, m.p. 138-139° after repeated recrystallization.

Found %: C 44.08; H 4.24; N 6.94; Cl 17.35
$C_{15}H_{18}O_7N_2Cl_2$. Calculated %: C 44.24; H 3.96; N 6.88; Cl 17.41

DL-threo-2-Amino-1-p-nitrophenyl-1,3-propanediol (IX). DL-threo-2-(2,2-Dichloroacetamido)-1-p-nitrophenyl-1,3-propanediol diacetic ester (1.02 g, i.e. 0.0025 mole) was boiled for four hours with 12 ml of 5% hydrochloric acid. The mixture was cooled and extracted with two 12-ml portions of ether. The aqueous phase was freed from traces of ether and made slightly alkaline (pH 8.5) with 40% caustic soda solution. Very quickly 0.455 g (86.5%) of white crystals of DL-threo-2-amino-1-p-nitrophenyl-1,3-propanediol (IX), m.p. 129-131° appeared. Recrystallization from water raised the melting point to 142-143°.

DL-Chloramphenicol (Levomycetin, Synthomycin). DL-threo-2-(2,2-Dichloroacetamido)-1-p-nitrophenyl-1,3-propanediol (VIIIa). a) DL-threo-2-Amino-1-p-nitrophenyl-1,3-propanediol (IX) (2.12 g, i.e. 0.01 mole) was dissolved in 40 ml of ethanol, and 2 ml of a 30% solution of HCl in absolute ether was added. The solution was evaporated to dryness, and the residue was dissolved in 24 ml of water. Methyl dichloroacetate (8 ml) was added, and the mixture was stirred vigorously at 8-10° while 4.5 ml of 36% caustic soda solution was added over a period of 50 minutes in such a way that the pH of the reaction mixture remained between 6 and 8. After reaction had been proceeding for ten minutes, 5 ml of methanol was added. After the addition of alkali was complete, the solution was freed from methanol at 40° and 2 mm pressure and was then extracted with six 20-ml portions of ethyl acetate. The extract was dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. The light-yellow oily residue was dissolved in 8 ml of hot ethyl acetate and caused to crystallize by addition of 4 ml of petroleum ether. The product was 2.23 g (72%) of DL-threo-2-(2,2-dichloroacetamido)-1-p-nitrophenyl-1,3-propanediol (VIIIa), melting after recrystallization at 152-153°. There was no depression in a mixture test with authentic chloramphenicol [6].

Found %: C 40.72; H 3.86; N 8.78; Cl 22.12
$C_{11}H_{12}O_5N_2Cl_2$. Calculated %: C 40.88; H 3.74; N 8.67; Cl 21.95

b) DL-threo-2-(2,2-Dichloroacetamido)-1-nitrophenyl-1,3-propanediol diacetic ester (1 g, i.e. 0.0025 mole) was dissolved in 50 ml of acetone. The solution was cooled to −7 to −8° and was stirred vigorously while 100 ml of 0.1 N NaOH, cooled to +2°, was added dropwise. The temperature of the solution was maintained at −10° for the next two hours. The solution was then titrated to Methyl orange with 0.2 N HCl. Acetone was removed at 2 mm pressure (30°), and the residue was extracted with ten 50-ml portions of ethyl acetate. The extract was dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. Two recrystallizations of the oily residue from ethyl acetate yielded 0.62 g of DL-threo-2-(2,2-dichloroacetamido)-1-p-nitrophenyl-1,3-propanediol (VIIIa), m.p. 151-153°, undepressed by admixture of authentic chloramphenicol [6].

c) The nitrate of DL-threo-O^3-acetyl-O^1-(dichloroacetyl)-2-amino-1-phenyl-1,3-propanediol (VIb) (10 g) was added at 0-5° with vigorous stirring to 30 ml of nitric acid (sp. gr. 1.52). After one hour the reaction mixture was poured into cold water containing potassium bicarbonate and calcium carbonate. The reaction product was extracted with five 50-ml portions of chloroform. The chloroform solution, after being dried and evaporated, yielded 4.02 g of an oily residue, which was dissolved in 220 ml of acetone. Cooled 0.1 N NaOH (440 ml) was added dropwise at −7 to −8°, and the mixture was maintained at −14° for two hours, after which it was neutralized with 0.2 N HCl. Acetone was removed at 30° (2 mm), and the residue was extracted with ten 60-ml portions of ethyl acetate. The extract was dried over anhydrous sodium sulfate, filtered, and evaporated. The oily residue was crystallized from 30 ml of 1 : 1 mixture of absolute ethyl acetate and absolute petroleum ether. The product was 2.12 g (25.5%) of DL-threo-2-(2,2-dichloroacetamido)-1-p-nitrophenyl-1,3-propanediol (VIIIa), m.p. 151-153.5°, undepressed by admixture with authentic chloramphenicol [6].

This investigation was aided by gifts of materials from the "Quinoin" pharmaceutical works and the Research Institute of the Pharmaceutics Industry. Microanalyses were carried out in our department by Dr. Eva Fodor-Varga, K. Lang, and R. Minarovich, with the help of technicians Imre Sabo and Lyuda Sabadi.

LITERATURE CITED

[1] V. Bruckner, Ann. 518, 226 (1935).

[2] V. Bruckner; A. Kramli, J. Prakt. Chem. 143, 2, 288(1935); 148. 5. 177 (1937).

[3] V. Bruckner, G. Fodor, Ber. 76, 466 (1943); G. Fodor, Ber. 76, 121 (1943); V. Bruckner, G. Fodor, J. Kiss, J. Kovacs, J. Chem. Soc. 1948, 885; G. Fodor, J. Kiss, M. Szerkerke, J. org. Chem. 15, 227 (1950). I. Kovacs, Pseudonitrosites of some Derivatives of Cinnamyl Alcohol, Doctorate Thesis, Szeged, 1943.

[4] E. Cherbuliez, Fr. Neumeir, H. Lozeron, Helv. 14, 191 (1931).

[5] Lott, U.S.Pat. 2103266.

[6] J. Controulis, M. C. Rebstock, H. M. Crooks, J. Am. Chem. Soc. 71, 2463 (1949).

[7] I. Kollonich, Report on Conference of the Society of Hungarian Chemists, Debreczen, 27. IX, 1953.

[8] L. M. Long, H. D. Troutman, J. Am. Chem. Soc., 71, 2469 (1949).

[9] a) G. Fodor, J. Kiss, Nature 163, 287 (1944); b) G. Fodor, J. Kiss, G. Ohegyi, J. org. Chem. 14, 336 (1949); c) G. Fodor, J. Kiss, M. Szekerke, J. org. Chem. 15, 227 (1950).

[10] G. Fodor, J. Kiss, L. Sallay, Nature 167, 690 (1951); J. Chem. Soc. 1951, 1858.

[11] K. Freudenberg, E. Schoffel, E. Braun, J. Am. Chem. Soc. 54, 234 (1932).

[12] K. J. Freudenberg, F. Nikolai, Ann. 510, 223 (1934); Leithe, Ber. 65, 660 (1932).

[13] K. Mislow, J. Am. Chem. Soc. 73, 3954 (1951).

[14] G. Carrara, G. Weitnauer, Gazz. Chim. Ital. 79, 856 (1949).

[15] K. Vogler, Helv. 33, 2111 (1950).

[16] J. D. Dunitz and J. E. Leonard, J. Am. Chem. Soc. 72, 4276 (1950).

[17] N. A. Preobrazhensky and E. I. Genkin, Chemistry of Organic Drugs. Satate Chem. Press, Moscow, 1953, pp. 545-546.

[18] a) Berichte Schimmel and Co. 1922, 5-166; C. 1929, IV, 764; b) M. Bourguel, Bull. 45. [4], 1067 (1929).

Received January 3, 1955

Institute of Organic Chemistry
Szeged University
Hungary

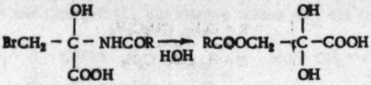
BLANK
PAGE

REACTIONS OF MERCAPTO AMINO ACIDS

COMMUNICATION 7. REACTIONS OF N-ACYL-2,3-DIHALOALANINES. (ACYLOXY)PYRUVIC ACIDS

O. V. Kildisheva, M. G. Linkova, and I. L. Knunyants

In a previous communication [1] we have described the formation and properties of N-acyl-3-halo-2-hydroxyalanines. Further investigation of the properties of these acids has shown that they are readily converted into new (acyloxy)pyruvic acids. When 3-bromo-2-hydroxy-N-(phenylacetyl)alanine and N-benzoyl-3-bromo-2-hydroxyalanine were treated with aqueous sodium bicarbonate, at first the acids were dissolved, and then the sparingly soluble sodium salts of the corresponding (acyloxy)pyruvic acids were precipitated; and from these the free acids (I and II) were liberated in the form of their hydrates by the action of 25% sulfuric acid.

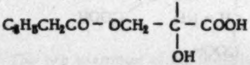
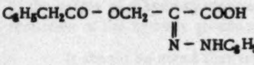
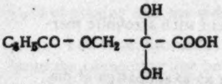
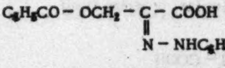


$$BrCH_2-\underset{COOH}{\overset{OH}{C}}-NHCOR \xrightarrow[HOH]{} RCOOCH_2-\underset{OH}{\overset{OH}{C}}-COOH$$

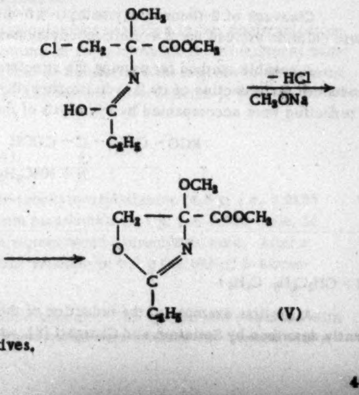
($R = C_6H_5,\ CH_2C_6H_5$).

(Acyloxy)pyruvic acids are readily soluble in water and in most organic solvents. They can be recrystallized from chloroform or dichloroethane. In alkaline solution they give the reddish-violet color characteristic for hydroxypyruvic acid. 2-4-Dinitrophenylhydrazine immediately gives precipitates of the corresponding 2,4-dinitrophenylhydrazones (III) and (IV), identical with the 2,4-dinitrophenylhydrazones obtained by acid hydrolysis of N-acyl-2,3-dibromoalanines [2].

TABLE

(Acyloxy)pyruvic acids and their 2,4-dinitrophenylhydrazones		M.p. (°C)
 $C_6H_5CH_2CO-OCH_2-\underset{OH}{\overset{OH}{C}}-COOH$	(I)	57 – 58
 $C_6H_5CH_2CO-OCH_2-\underset{N-NHC_6H_3(NO_2)_2}{\underset{\Vert}{C}}-COOH$	(III)	169 – 170
 $C_6H_5CO-OCH_2-\underset{OH}{\overset{OH}{C}}-COOH$	(II)	68 – 70
 $C_6H_5CO-OCH_2-\underset{N-NHC_6H_3(NO_2)_2}{\underset{\Vert}{C}}-COOH$	(IV)	168 – 173

Investigation of the methyl ester of N-benzoyl-3-chloro-2-methoxyalanine [1] has shown that the conversion of N-acyl-2,3-dihaloalanines and N-acyl-3-halo-2-hydroxyalanines into derivatives of (acyloxy)pyruvic acids proceeds through the intermediate formation of oxazoline derivatives. When the methyl ester of N-benzoyl-3-chloro-2-methoxyalanine was treated with an equimolecular amount of sodium methoxide, the methyl ester of 4-methoxy-2-phenyl-2-oxazoline-4-carboxylic acid (V), m.p. 56°, was isolated.

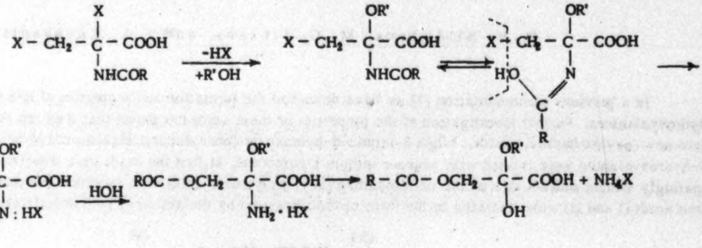


(V)

As might be expected, the oxazoline (V) was found to be extremely sensitive toward acids. Thus, we were able to isolate the stable sodium salt of 4-methoxy-2-phenyl-2-oxazoline-4-carboxylic acid after hydrolysis of the ester group, but all attempts to convert this into the free acid were unsuccessful. Acidification of the sodium salt resulted in cleavage of the oxazoline ring and the only final hydrolysis product was the (acyloxy)pyruvic acid. Hence, in reactions in aqueous media both N-acyl-2,3-dibromoalanines and N-acyl-3-bromo-2-hydroxyalanines generally yield hydroxypyruvic acid or its derivatives.

N-Acyl-2,3-dichloroalanines and N-acyl-3-chloro-2-hydroxyalanines were found to be more stable to hydrolysis, and the conversion of N-benzoyl-3-chloro-2-hydroxyalanine, for example, was found to occur only under the action of a stronger base (N NaOH).

The fact of the formation of the methyl ester of 4-methoxy-2-phenyl-2-oxazoline –4–carboxylic acid enables us to represent the conversion of halogen derivatives of N-acylalanines into derivatives of (acyloxy)pyruvic acids in the following way:

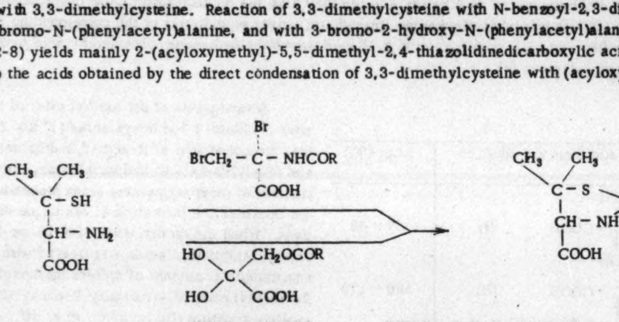


R = C_6H_5, $CH_2C_6H_5$

R' = H, CH_3, C_2H_5

A certain analogy to the rearrangement that we have observed is to be found in the migration of an acyl group from nitrogen to oxygen in hydroxy amines [3, 4, 5].

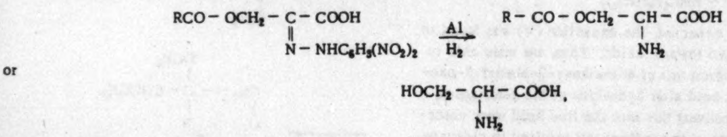
The above-described transformations of N-acyl-2,3-dihaloalanines occur also when these compounds are condensed with 3,3-dimethylcysteine. Reaction of 3,3-dimethylcysteine with N-benzoyl-2,3-dibromoalanine, with 2,3-dibromo-N-(phenylacetyl)alanine, and with 3-bromo-2-hydroxy-N-(phenylacetyl)alanine over a wide pH range (2-8) yields mainly 2-(acyloxymethyl)-5,5-dimethyl-2,4-thiazolidinedicarboxylic acids (VI and VII), identical to the acids obtained by the direct condensation of 3,3-dimethylcysteine with (acyloxy)pyruvic acids:



(VI) R = $CH_2C_6H_5$; (VII) R = C_6H_5.

Cleavage of 2-(benzoyloxymethyl)-5,5-dimethyl-2,4-thiazolidinedicarboxylic acid with alcoholic mercuric chloride yielded the 2,4-dinitrophenylhydrazone of (benzoyloxy)pyruvic acid.

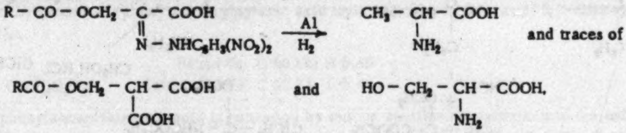
A possible method for proving the structure of the (acyloxy)pyruvic acid would be an examination of the products of the reduction of its 2,4-dinitrophenylhydrazone, which should yield an O-acylserine, or serine itself if reduction were accompanied by hydrolysis of the ester grouping:



(R = $CH_2C_6H_5$; C_6H_5).

A similar example of the reduction of the 2,4-dinitrophenylhydrazone of hydroxypyruvic acid was recently described by Sprinsson and Chargaff [6], who did in fact isolate serine in 30% yield. In contrast with this experiment on the reduction of the 2,4-dinitrophenylhydrazone of hydroxypyruvic acid, the reduction of the 2,4-dinitrophenylhydrazones of (acyloxy)pyruvic acid, that we have prepared unexpectedly resulted in the isolation of alanine. This result caused us to make a more detailed study of the reduction products, not only those formed in Sprinsson and Chargaff's experiment, but also those obtained from the 2,4-dinitrophenylhydrazones of (acyloxy)-pyruvic acid.

An investigation of the reduction products obtained in these reactions with the aid of partition chromatography showed that in the reduction of 2,4-dinitrophenylhydrazones of (acyloxy)pyruvic acids, not only alanine – the main reaction product – but also serine and O-acylserine were formed:

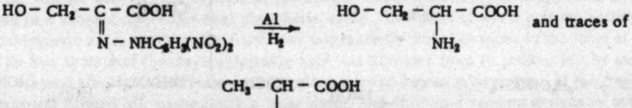


$$R-CO-OCH_2-\underset{\underset{N-NHC_6H_3(NO_2)_2}{\|}}{C}-COOH \xrightarrow[H_2]{Al} CH_3-\underset{\underset{NH_2}{|}}{CH}-COOH \quad \text{and traces of}$$

$$RCO-OCH_2-\underset{\underset{COOH}{|}}{CH}-COOH \quad \text{and} \quad HO-CH_2-\underset{\underset{NH_2}{|}}{CH}-COOH,$$

($R = CH_2C_6H_5,\ C_6H_5$).

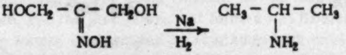
In the reduction of the 2,4-dinitrophenylhydrazone of hydroxypyruvic acid, the main reaction product is indeed serine, as stated by Sprinsson and Chargaff [6], but alanine, which they did not detect, is also present:



$$HO-CH_2-\underset{\underset{N-NHC_6H_3(NO_2)_2}{\|}}{C}-COOH \xrightarrow[H_2]{Al} HO-CH_2-\underset{\underset{NH_2}{|}}{CH}-COOH \quad \text{and traces of}$$

$$CH_3-\underset{\underset{NH_2}{|}}{CH}-COOH$$

Thus, in this investigation we have found examples of the reduction of hydroxymethyl and acyloxymethyl groups to CH_3 groups by aluminum amalgam. This result is the consequence of the structural peculiarities of hydrazones of hydroxypyruvic acid. Unlike the hydrazones of (acyloxy)- and hydroxy-pyruvic acids, O-acylserine does not yield alanine under the same conditions. Hence, the presence of the α-hydrazone grouping greatly affects the character of the hydroxy or acyloxy group, making them capable of undergoing exhaustive reduction (to the CH_3 group) under conditions under which alcohols and esters are not reduced. Similar behavior has been observed by Piloty and Ruff [7], who obtained isopropylamine by the reduction of the oxime of dihydroxyacetone:



$$HOCH_2-\underset{\underset{NOH}{\|}}{C}-CH_2OH \xrightarrow[H_2]{Na} CH_3-\underset{\underset{NH_2}{|}}{CH}-CH_3$$

The two examples of the reduction of hydroxy and acyloxy groups found in this investigation and the reduction of the oxime of dihydroxyacetone to isopropylamine are examples of what is probably a general rule of the ready reduction of the hydroxy groups of oximes and hydrazones of α-hydroxy carbonyl compounds.

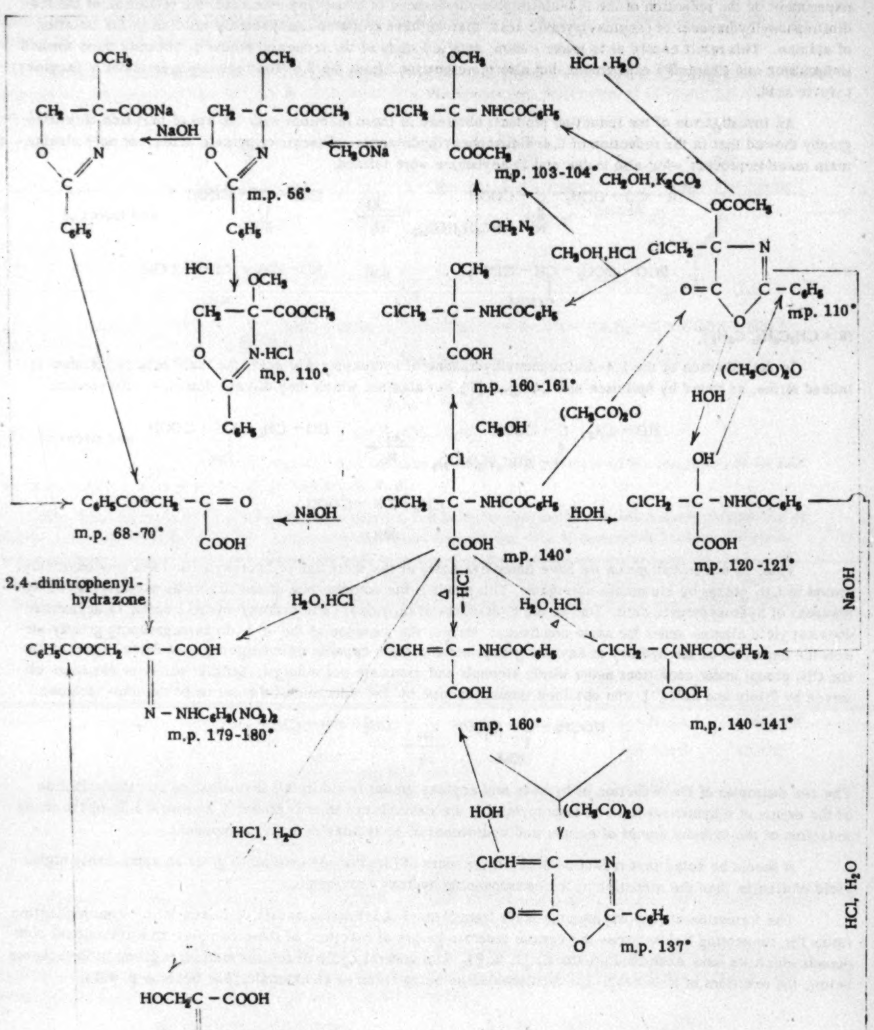
It should be noted that reduction of the hydrazones of (acyloxy)pyruvic acids gives an appreciably higher yield of alanine than the reduction of the corresponding hydroxy compounds.

The formation of (acyloxy)pyruvic acids from N-acyl-2,3-dihaloalanines described in this communication forms the connecting link between the various separate groups of reactions of these complex multifunctional compounds which we have examined previously [1, 2, 8]. The general cycle of transformations is given in the scheme below, the reactions of N-benzoyl-2,3-dichloroalanine being taken as an example. (See Scheme p. 404).

EXPERIMENTAL

Hydrate of (Phenylacetoxy)pyruvic Acid (I). 2,3-Dibromo-N-(phenylacetyl)alanine (4.5 g, i.e. 0.0125 mole) was treated with excess of a saturated aqueous solution of sodium bicarbonate (2.1 g, i.e. 0.025 mole, in 20 ml of water). The alkaline solution was acidified to pH 1.5 with concentrated hydrochloric acid. After a short time the crystalline precipitate that formed was filtered off. The product was 0.9 g (24.0%) of 3-bromo-2-hydroxy-N-(phenylacetyl)alanine, m.p. 105-106°.

The acid mother liquor was evaporated to dryness under reduced pressure. The residue was extracted with ether. Ether was allowed to evaporate until crystallization began. The crystals were filtered off, washed with a


OCH3
CH2 — C — COONa
O N
C
C6H5
NaOH
OCH3
CH2 — C — COOCH3
O N
C
m.p. 56°
C6H5
CH3ONa
OCH3
ClCH2 — C — NHCOC6H5
COOCH3
m.p. 103-104°
HCl · H2O
CH3OH, K2CO3
OCOCH3
ClCH2 — C — N
O=C C — C6H5
O
m.p. 110°
CH2N2
CH3OH, HCl
HCl
OCH3
CH2 — C — COOCH3
O N·HCl
C
m.p. 110°
C6H5
OCH3
ClCH2 — C — NHCOC6H5
COOH
m.p. 160-161°
(CH3CO)2O
HOH
(CH3CO)2O
CH3OH
Cl
ClCH2 — C — NHCOC6H5
COOH
m.p. 140°
HOH
OH
ClCH2 — C — NHCOC6H5
COOH
m.p. 120-121°
C6H5COOCH2 — C = O
COOH
m.p. 68-70°
NaOH
NaOH
2,4-dinitrophenylhydrazone
H2O, HCl
− HCl
Δ
H2O, HCl
Δ
C6H5COOCH2 — C — COOH
N — NHC6H3(NO2)2
m.p. 179-180°
ClCH = C — NHCOC6H5
COOH
m.p. 160°
ClCH2 — C(NHCOC6H5)2
COOH
m.p. 140-141°
HOH
(CH3CO)2O
ClCH = C — N
O = C C — C6H5
O
m.p. 137°
HCl, H2O
HCl, H2O
HOCH2C — COOH
N — NHC6H3(NO2)2
m.p. 160-161°

little benzene, and then chloroform, and finally crystallized from chloroform. The product was 0.5 g (17%) of the hydrate of (phenylacetoxy)pyruvic acid in the form of petal-shaped crystals, m.p. 57-58°.

Found %: C 54.87; H 4.93
$C_{11}H_{12}O_6$. Calculated %: C 55.00; H 5.0

The hydrate of (phenylacetoxy)pyruvic acid was found to be very soluble in water, alcohol, and ether, and it readily crystallized from chloroform and dichloroethane. In alkaline solution it gave a reddish-violet color with ferric chloride. With a 0.5% solution of 2,4-dinitrophenylhydrazine in 2N HCl an aqueous solution of the hydrate of (phenylacetoxy)pyruvic acid immediately gave a crystalline hydrazone, m.p. 168-170° (from alcohol), identical with the 2,4-dinitrophenylhydrazone of (phenylacetoxy)pyruvic acid isolated in the hydrolysis of 2,3-dibromo-N-(phenylacetyl)alanine [2].

Found %: C 50.52; H 3.49
$C_{17}H_{14}O_8N_4$. Calculated %: C 50.74; H 3.48

The hydrate of (phenylacetoxy)pyruvic acid is converted by sodium bicarbonate solution into the sodium salt, which is sparingly soluble in water. The free acid is liberated when the salt is treated with 25% sulfuric acid.

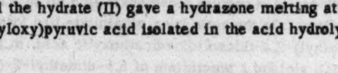
Hydrate of (Benzoyloxy)pyruvic Acid (II). N-Benzoyl-2,3-dibromoalanine (8 g, i.e. 0.022 mole) was treated with a saturated aqueous solution of sodium bicarbonate (3 g, i.e. 0.037 mole, in 30 ml of water). The precipitate was filtered off; it consisted of 2.7 g (44.2%) of N-benzoyl-3-bromo-2-hydroxyalanine, m.p. 92-93°. The filtrate was set aside in a refrigerator. On the next day the crystalline precipitate was filtered off (yielding Filtrate I), washed with a little water, and dried in a vacuum desiccator over phosphoric oxide. The product was 2 g of the sodium salt of the hydrate of (benzoyloxy)pyruvic acid, which crystallized very satisfactorily from hot water in the form of clear gleaming crystals. The free hydrate of (benzoyloxy)pyruvic acid was liberated from its sodium salt by means of 25% sulfuric acid. A day elapsed after the acidification of the clear solution before a precipitate of the free acid formed. The precipitate was filtered off, washed with a little water, and dried in a vacuum desiccator over phosphoric oxide. The product was 0.7 g of the hydrate of (benzoyloxy)pyruvic acid, m.p. 68-70° (from chloroform).

Found %: C 52.88; H 4.47
$C_{10}H_{10}O_6$. Calculated %: C 53.0; H 4.42

The hydrate (II) was found to be readily soluble in water, alcohol, and ether, and could be crystallized from chloroform and dichloroethane. With ferric chloride an alkaline solution of the hydrate of (benzoyloxy)pyruvic acid gave the reddish-violet color that is characteristic for hydroxypyruvic acid. When the solution was heated for three minutes with 0.5 N NaOH, the reaction with ferric chloride was no longer given. The solution was cooled and acidified with 25% sulfuric acid, and the precipitate that formed was filtered off and dried. The product was benzoic acid, m.p. 121-122° (from water), undepressed by admixture with known benzoic acid. With a 0.5% solution of 2,4-dinitrophenylhydrazine in 2 N HCl the hydrate (II) gave a hydrazone melting at 168-173°, identical with the 2,4-dinitrophenylhydrazone of (benzoyloxy)pyruvic acid isolated in the acid hydrolysis of N-benzoyl-2,3-dibromoalanine [2].

Found %: C 49.36; H 3.17; N 14.37
$C_{16}H_{12}O_8N_4$. Calculated %: C 49.48; H 3.09; N 14.4

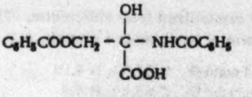
Filtrate I was evaporated to dryness under reduced pressure, and the residue was treated with 25% sulfuric acid and extracted with ether. The ether extract was dried over anhydrous sodium sulfate and evaporated until crystallization began. The precipitate was filtered off and found to be 1.1 g of a substance with an extended melting range. After repeated reprecipitation from a sodium bicarbonate solution with acid and fractional crystallization of the sodium salts from water, we succeeded in isolating some more hydrate of (benzoyloxy)pyruvic acid, m.p. 68-70° (0.2 g; the total yield of the hydrate (II) was 17.6%) and also the new 2,2-bis(benzamido)-3-bromopropionic acid, m.p. 124°:



$$BrCH_2-\underset{\displaystyle COOH}{\underset{|}{C}}-(NHCOC_6H_5)_2$$

Found %: C 52.3; H 4.07; N 7.59; Br 21.47
$C_{17}H_{15}O_4N_2Br$. Calculated %: C 52.1; H 3.83; N 7.2; Br 22.4

In addition to this an acid having a double melting point, 90° and 114°, was isolated. It was close in properties to the hydrate of (benzoyloxy)pyruvic acid, but contained nitrogen. It is probable that it was inadequately purified N-benzoyl-3-(benzoyloxy)-2-hydroxyalanine:



$$C_6H_5COOCH_2-\overset{\displaystyle OH}{\underset{\displaystyle COOH}{\overset{|}{\underset{|}{C}}}}-NHCOC_6H_5$$

Found %: N 4.17

$C_{17}H_{15}O_6N$. Calculated %: N 4.25

With a 0.5% solution of 2,4-dinitrophenylhydrazine in 2 N HCl the acid melting at 90° and 114° gave a 2,4-dinitrophenylhydrazone melting at 168-170°. A mixture test with the 2,4-dinitrophenylhydrazone of (benzoyloxy)pyruvic acid showed no depression.

Methyl Ester of 4-Methoxy-2-phenyl-2-oxazoline-4-carboxylic Acid (V). A solution of 0.54 g (0.002 mole) of the methyl ester of N-benzoyl-3-chloro-2-methoxyalanine in 5 ml of absolute methanol was mixed with 2.4 ml of a solution of sodium methoxide (0.002 mole). After two hours at room temperature the solution was evaporated to dryness under reduced pressure. The residue was extracted with absolute ether, and the ether was distilled off. The product was the methyl ester of 4-methoxy-2-phenyl-2-oxazoline-4-carboxylic acid, m.p. 56°.

Found %: C 61.29; H 5.47; N 6.07

$C_{12}H_{13}NO_4$. Calculated %: C 61.27; H 5.50; N 5.95

Treatment of (V) with alcoholic HCl in absolute ether gave a crystalline hydrochloride, m.p. 110°, which decomposed very readily.

Sodium Salt of 4-Methoxy-2-phenyl-2-oxazoline-4-carboxylic Acid. To 0.27 g (0.001 mole) of the methyl ester of N-benzoyl-3-chloro-2-methoxyalanine in 2 ml of methanol, 1 ml of 2 N methanolic NaOH (0.002 mole) was added, and the mixture was set aside for two hours at room temperature. Precipitated sodium chloride was filtered off, and the filtrate was evaporated to half bulk under reduced pressure. The precipitated sodium salt of 4-methoxy-2-phenyl-2-oxazoline-4-carboxylic acid was filtered off and washed with a little alcohol. The product was 0.15 g of the sodium salt of 4-methoxy-2-phenyl-2-oxazoline-4-carboxylic acid.

Found %: N 5.38

$C_{11}H_{10}NO_4Na$. Calculated %: N 5.75

The sodium salt of 4-methoxy-2-phenyl-2-oxazoline-4-carboxylic acid was found to be readily soluble in alcohol and in water. It was not found possible to isolate the free acid from the sodium salt; when an aqueous solution was acidified with the equivalent amount of sulfuric acid, after some time a precipitate of the sodium salt of (benzoyloxy)pyruvic acid formed.

5,5-Dimethyl-2-(phenylacetoxymethyl)-2,4-thiazolidinedicarboxylic Acid (VI). 3-Bromo-2-hydroxy-N-(phenylacetyl)alanine (0.6 g, i.e. 0.002 mole) was added to a solution of 0.3 g (0.002 mole) of 3,3-dimethylcysteine and 0.16 g (0.002 mole) of sodium bicarbonate in 5 ml of water. The mixture (pH 4) was set aside for 12 hours at room temperature. On the next day a precipitate had formed of the monosodium salt of 5,5-dimethyl-2-(phenylacetoxymethyl)-2,4-thiazolidinedicarboxylic acid, m.p. 187-190° (dec.). Acidification of the mother liquor with N H_2SO_4 yielded a precipitate of 5,5-dimethyl-2-(phenylacetoxymethyl)-2,4-thiazolidinedicarboxylic acid, readily soluble in alcohol, ether, and acetone, sparingly soluble in benzene and chloroform. The acid was purified by dissolving it in acetone, adding an equal volume of water, and leaving the solution to the next day. The acid (VI) then melted with decomposition at 166-167°.

Found %: C 53.9; H 5.5; S 9.1

$C_{16}H_{19}O_6NS$. Calculated %: C 54.3; H 5.3; S 9.06

The neutralization equivalent was found to be 177 (molecular weight 353).

The monosodium salt was acidified with sulfuric acid and yielded the free acid (VI), m.p. 167-168° (dec.). The total yield of the acid (VI) was 80%.

Similar results were obtained also with 2,3-dibromo-N-(phenylacetyl)alanine in presence of two molecular proportions of sodium bicarbonate. With excess of diazomethane in ether solution 5,5-dimethyl-2-(phenylacetoxymethyl)-2,4-thiazolidinedicarboxylic acid formed what appeared to be the dimethyl ester of 3,5,5-trimethyl-2-(phenylacetoxymethyl)-2,4-thiazolidinedicarboxylic acid, m.p. 101-102° (from ether).

Found %: C 58.02; H 6.6; S 8.14

$C_{19}H_{25}O_6NS$. Calculated %: C 57.7; H 6.3; S 8.1

2-(Benzoyloxymethyl)-5,5-dimethyl-2,4-thiazolidinedicarboxylic Acid (VII). a) N-Benzoyl-2,3-dibromoalanine (4.3 g, i.e. 0.012mole) was added to a solution of 1.9 g (0.012 mole) of 3,3-dimethylcysteine in 20 ml of water, and the mixture (pH 2) was set aside for 12 hours at room temperature. The precipitate formed was filtered off and washed with a little water. The product was 3.45 g (80,6%) of the acid (VII); 3 g of this was dissolved in 10 ml of acetone, 20 ml of water was added, and the mixture was set aside until the next day, when 2.5 g of the acid (VII) melting with decomposition at 165-166° was obtained.

2-(Benzoyloxymethyl)-5,5-dimethyl-2,4-thiazolidinedicarboxylic acid is readily soluble in alcohol, ether, and acetone, sparingly soluble in chloroform and cold water; it can be crystallized from hot water. In the cold it is insoluble in 2 N HCl, and at the boil it is decarboxylated. It may be titrated iodometrically in the same way as penicilloic acid [9].

Found %: C 52.7; H 5.2; S 9.3; N 4.3

$C_{15}H_{17}O_6NS$. Calculated %: C 53.0; H 5.0; S 9.4; N 4.1

b) To a solution of 1.5 g (0.01 mole) of 3,3-dimethylcysteine in 20 ml of water, 3 g (0.04 mole) of sodium bicarbonate and 3.4 g (0.01 mole) of N-benzoyl-2,3-dibromoalanine were added. The mixture was set aside at room temperature for 12 hours, and was then heated for five hours at 40° (pH 8). The ferric chloride test for the mercapto group was positive. The mixture was cooled, and the precipitate present was filtered off and washed with water. The product was 0.8 g of the sodium salt of the hydrate of (benzoyloxy)pyruvic acid. Acidification of the mother liquor with N H_2SO_4 gave a very slight precipitate of 2-(benzoyloxymethyl)-5,5-dimethyl-2,4-thiazolidinedicarboxylic acid.

Treatment of the sodium salt of the hydrate of (benzoyloxy)pyruvic acid with 25% sulfuric acid yielded the free hydrate of the acid, m.p. 68-70° (from chloroform), identical with the hydrate (II). When 2-(benzoyloxymethyl)-5,5-dimethyl-2,4-thiazolidinedicarboxylic acid was treated with mercuric chloride in presence of 2,4-dinitrophenylhydrazine, the hydrazone of (benzoyloxy)pyruvic acid, m.p. 167-168° and identical with the hydrazone (IV), was obtained.

Reduction of 2,4-Dinitrophenylhydrazones Derived from Pyruvic Acid. 1) A suspension of 3.8 g (0.01 mole) of the 2,4-dinitrophenylhydrazone of (benzoyloxy)pyruvic acid in 100 ml of 80% ethanol was treated with freshly prepared activated aluminum (prepared with the aid of $HgCl_2$ by Adkin's method from 10 g of aluminum). The mixture was stirred at 20° for 30 minutes, and stirring was continued overnight at room temperature. On the next day the dark-brown solution was filtered, and the aluminum hydroxide was carefully washed on the filter with 300 ml of hot water. The dark-brown solution was decolorized with animal charcoal and evaporated to dryness under reduced pressure. The residue was dissolved in the least possible volume of water, absolute alcohol was added until a turbidity appeared, and the mixture was set aside in a refrigerator. On the next day the crystalline precipitate was filtered off and dried; it was 0.25 g (28%) of alanine, melting with decomposition at 290-292° and showing no depression in a mixture test with known alanine. The mother liquor from the alanine separation was evaporated to dryness at room temperature, and the residue was dissolved in the least possible amount of water and analyzed by partition chromatography on paper. The developed chromatogram showed the presence of alanine, serine, and O-benzoylserine.

2) The 2,4-dinitrophenylhydrazone of (phenylacetoxy)pyruvic acid (1 g) was reduced with amalgamated aluminum in the manner described above. The solution, after decolorization with charcoal, was evaporated to low bulk and analyzed by partition chromatography on paper. The developed chromatogram showed the presence of alanine, serine, and O-(phenylacetyl)serine.

3) The above-described method of reduction with amalgamated aluminum was applied to 1 g of the 2,4-dinitrophenylhydrazone of hydroxypyruvic acid (prepared by Sprinsson's method [6] from bromopyruvic acid). The solution, after evaporation to low bulk, was analyzed by partition chromatography on paper. The developed chromatogram showed the presence not only of serine, but also of alanine.

4) O-Benzoylserine (0.7 g) was subjected to the aluminum-amalgram reduction treatment described above for the 2,4-dinitrophenylhydrazone of (benzoyloxy)pyruvic acid. Only serine was isolated, and no other substance was detected on the chromatogram.

SUMMARY

1. It is shown that, over a wide pH range, N-acyl-2,3-dihaloalanines are converted by water into (acyloxy)pyruvic acids with intermediate formation of 2-aryl(or alkyl)-4-hydroxy-2-oxazoline-4-carboxylic acids.

2. It is shown that the ability of α-acetoxy and α-hydroxy groups in hydrazones and oximes of α-hydroxy carbonyl compounds to undergo exhaustive reduction when treated with metal amalgams and water forms a general rule.

LITERATURE CITED

[1] O. V. Kildisheva, M. G. Linkova, and I. L. Knunyants, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 2, 271.*

[2] O. V. Kildisheva, L. P. Rasteiken, and I. L. Knunyants, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 2, 260.**

[3] M. Bergmann, A. Mickely, Z. phys. Chem. 140, 128 (1924).

[4] E. Fry, J. org. Chem. 14, 887 (1949); 15, 438 (1950).

[5] E. Baltazz et al., Chem. Ind. No. 22, 541 (1953).

[6] D. Sprinsson, E. Chargaff, J. Biol. Chem. 164, 417 (1946).

[7] Piloty, O. Ruff, Ber. 30, 1664 (1897).

[8] O. V. Kildisheva, M. G. Linkova, and I. L. Knunyants, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 2, 282.***

[9] J. Alicino, Ind. Eng. Chem. (Anal. Ed.), 18, No. 20, 619, 1946.

Received April 9, 1954

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

---

* Consultant's Bureau Translation, p 241.

** Consultant's Bureau Translation, p 231.

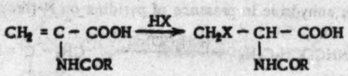
*** Consultant's Bureau Translation, p 251.

REACTIONS OF MERCAPTO AMINO ACIDS

COMMUNICATION 8. ALKYLATION AND ACYLATION OF CYSTEINE AND 3,3-DIMETHYLCYSTEINE BY DERIVATIVES OF N-ACYL-3-HALOALANINES

I. L. Knunyants and V. V. Shokina

It was shown in a previous communication [1] that 3,3-dimethylcysteine is readily alkylated by halo carboxylic acids and readily acylated by acid chlorides. In the present investigation we have studied the acylation and alkylation of cysteine and 3,3-dimethylcysteine by more complex derivatives of carboxylic acids containing both a halogen and an acylamino group, such as N-acyl-3-haloalanines. Only very few acids of this type are known, and these are prepared by complex transformations of the difficultly accessible serine [2, 3, 4, 5, 6]. In the present communication it is shown that N-acyl-3-haloalanines can be prepared by addition of hydrogen bromide or hydrogen chloride to 2-(acylamino)acrylic acids [7]:



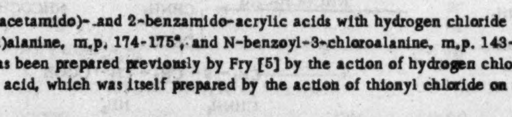
$$CH_2=\underset{NHCOR}{\underset{|}{C}}-COOH \xrightarrow{HX} CH_2X-\underset{NHCOR}{\underset{|}{CH}}-COOH$$

X = Cl, Br; R = C_6H_5, $CH_2C_6H_5$.

By the action of a solution of hydrogen bromide in glacial acetic acid on 2-(2-phenylacetamido)acrylic acid, 3-bromo-N-(phenylacetyl)alanine, m.p. 163°, was obtained in almost quantitative yield. In the preparation of N-benzoyl-3-bromoalanine considerable difficulties were met on account of the instability of 2-benzamidoacrylic acid. In presence of traces of moisture, arising from the acetic acid or from inadequately dried hydrogen bromide, the benzamido group was split off with formation of benzamide hydrobromide and derivatives of pyruvic acid. By taking all possible precautions we succeeded in obtaining N-benzoyl-3-bromoalanine, m.p. 136-137°, in 66% yield.

Treatment of 2-(2-phenylacetamido)- and 2-benzamido-acrylic acids with hydrogen chloride in dioxane yielded 3-chloro-N-(phenylacetyl)alanine, m.p. 174-175°, and N-benzoyl-3-chloroalanine, m.p. 143-144°, respectively. The last compound has been prepared previously by Fry [5] by the action of hydrogen chloride on 2-phenyl-2-oxazoline-4-carboxylic acid, which was itself prepared by the action of thionyl chloride on an ester of serine.

When treated with diazomethane, 3-bromo-N-(phenylacetyl)alanine is readily converted into its methyl ester, m.p. 87-89°. Treatment of the same compound with aqueous caustic alkali yields 2-(2-phenylacetamido) acrylic acid and the previously unknown O-(phenylacetyl)serine, m.p. 153°:



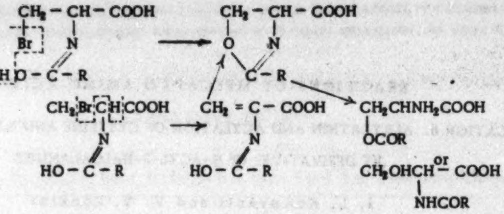
$$BrCH_2\underset{NHCOCH_2C_6H_5}{\underset{|}{CH}}-COOH \xrightarrow{NaOH} \begin{cases} \xrightarrow{\text{2 molecules}} CH_2=\underset{NHCOCH_2C_6H_5}{\underset{|}{C}}-COOH \\ \xrightarrow{\text{1 molecule}} \underset{O-COCH_2C_6H_5}{\underset{|}{CH_2}}-CHNH_2-COOH \end{cases}$$

The formation of an O-acyl derivative of serine is the result of complex transformations.

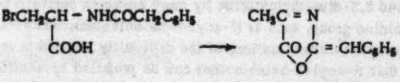
It is probable that at first an unstable oxazoline is formed, either by the elimination of HBr from the enol form of 3-bromo-N-(phenylacetyl)alanine or by elimination of HBr with formation of an acrylic acid derivative followed by addition of the enol hydroxyl at the double bond. Hydrolysis of the oxazoline, depending on the conditions (pH of medium), leads to an N- or O-acyl derivative of serine (See top of next page).

When 3-bromo-N-(phenylacetyl)alanine was heated with very dilute hydrobromic acid, serine was formed in 78% yield. This appears to be the best method of preparing serine. Under the same conditions N-benzoyl-3-bromoalanine was converted into O-benzoylserine, serine itself being obtained under more severe conditions (heating with 20% hydrochloric acid).

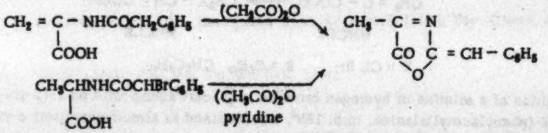
(formula from preceding page)



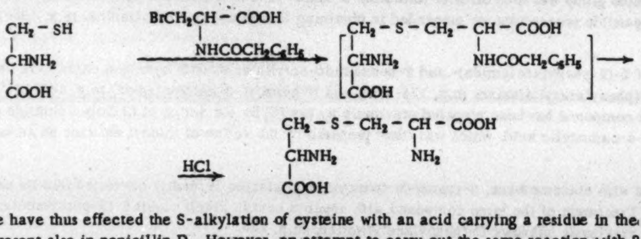
When attempts were made to prepare an acid chloride or mixed anhydride of 3-bromo-N-(phenylacetyl)-alanine by treatment with PCl$_5$, SOCl$_2$, or acetic anhydride, the product obtained was always 2-benzylidene-4-methyl-3-oxazolin-5-one, m.p. 129-131°:



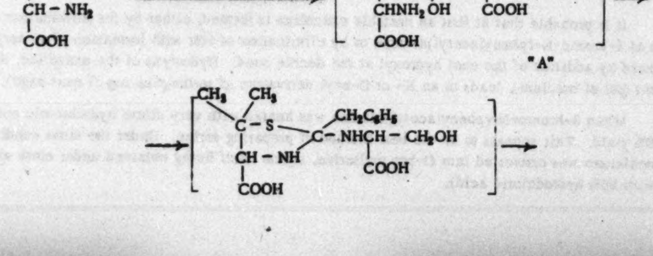
This 3-oxazolin-5-one has been prepared previously by the action of acetic anhydride on 2-(2-phenylacetamido) acrylic acid and by the action of acetic anhydride in presence of pyridine on N-[bromo(phenyl)acetyl]alanine [8]:

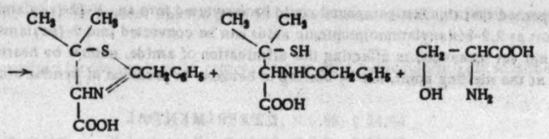


We proceeded to a study of the alkylation of mercapto amino acids with 3-bromo-N-(phenylacetyl) alanine. Reaction of the latter compound with cysteine gave a 50% yield of lanthionine:

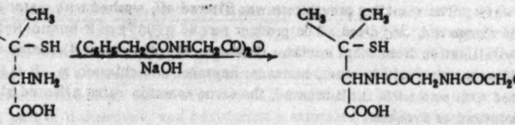


We have thus effected the S-alkylation of cysteine with an acid carrying a residue in the α-position which is present also in penicillin D. However, an attempt to carry out the same reaction with 3,3-dimethylcysteine gave unexpected results; instead of the expected S-alkylation, transacylation occurred, probably with intermediate formation of the unstable addition product "A", which undergoes decomposition in several directions under the action of acids. Reaction products isolated were serine, 3,3-dimethyl-N-(phenylacetyl)cysteine, and 2-benzyl-5,5-dimethyl-2-thiazoline-4-carboxylic acid, m.p. 140-141°:

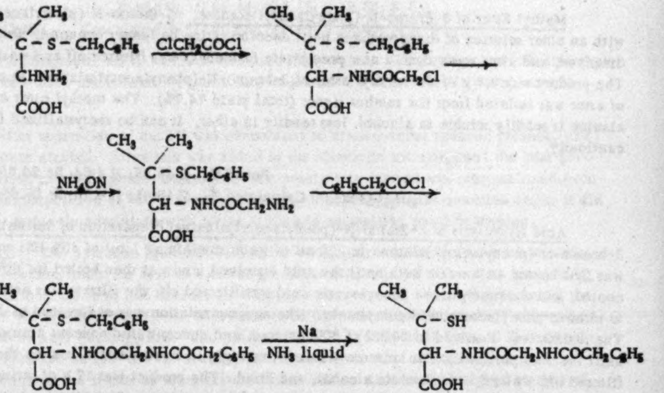




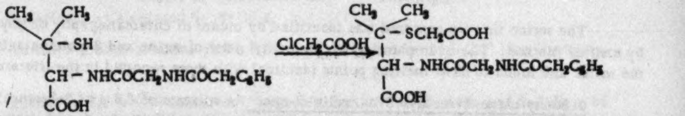
Further investigation showed that 3,3-dimethylcysteine is readily acylated with anhydrides of α-acylamino acids. Thus, under Schotten-Baumann conditions, 3,3-dimethyl-N-phenaceturylcysteine was readily obtained by the action of phenaceturic anhydride on 3,3-dimethylcysteine:



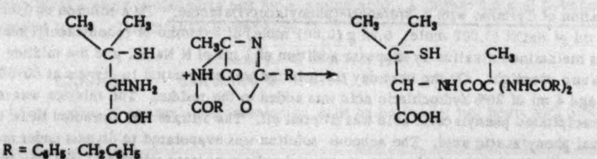
The product was identical with the 3,3-dimethyl-N-phenaceturylcysteine obtained by Süs [9] by the following sequence of reactions:



Treatment of 3,3-dimethyl-N-phenaceturylcysteine with chloroacetic acid yielded S-(carboxymethyl)-3,3-dimethyl-N-phenaceturylcysteine, which decomposed at 90°:



The reactions of 3,3-dimethylcysteine with saturated oxazolinones resulted in the preparation of new N-acylated derivatives of 3,3-dimethylcysteine. Thus, the acylation of 3,3-dimethylcysteine with 4-benzamido-4-methyl-2-phenyl-2-oxazolin-5-one [10] yielded N-(2,2-dibenzamidopropionyl)-3,3-dimethylcysteine, m.p. 203-204°. Acylation of 3,3-dimethylcysteine with 2-benzyl-4-methyl-4-(2-phenylacetamido)-2-oxazolin-5-one [11] yielded N-[2,2-bis(2-phenylacetamido)propionyl]-3,3-dimethylcysteine, m.p. 187-189°:



It was to be expected that this last compound could be converted into an N-[2-(acylamino)acryloyl]-3,3-dimethylcysteine, just as 2,2-bis(acylamino)propionic acids can be converted into 2-(acylamino)acrylic acids. However, we have not yet succeeded in effecting this elimination of amide, neither by heating in glacial acetic acid nor by heating at the melting point, nor by boiling in benzene in presence of pyruvic acid.

EXPERIMENTAL

3-Bromo-N-(phenylacetyl)alanine. 2-(2-Phenylacetamido)acrylic acid (10.5 g, i.e. 0.1 mole) was introduced into 70 ml of glacial acetic acid containing 18 g of hydrogen bromide. After one hour the whole of the acid had dissolved. The solution was set aside at room temperature until the next day, when it was poured into 200 ml of ice water. The resulting precipitate was filtered off, washed with water until there was no longer an acid reaction to Congo red, and dried. The product was 25 g (90%) of 3-bromo-N-(phenylacetyl)alanine, m.p. 163° after recrystallization from ethyl acetate. 3-Bromo-N-(phenylacetyl)alanine is readily soluble in alcohol, acetone, and dioxane, sparingly in ether, benzene, heptane, and chloroform. It is insoluble in cold water, and when it is heated with water HBr is eliminated, the same reaction being effected also by sodium bicarbonate, silver nitrate solution, or pyridine.

Found %: C 46.00; H 4.21; N 5.1; Br 28.24
$C_{11}H_{12}O_3NBr$. Calculated %: C 46.17; H 4.19; N 4.89; Br 27.93

Methyl Ester of 3-Bromo-N-(phenylacetyl)alanine. 3-Bromo-N-(phenylacetyl)alanine (6.5 g) was treated with an ether solution of diazomethane until decolorization no longer occurred. During the treatment the acid dissolved, and after some time a new precipitate formed; it was filtered off and washed with ether on the filter. The product was 3.4 g of the methyl ester of 3-bromo-N-(phenylacetyl)alanine, m.p. 87-89°. A further 2.1 g of ester was isolated from the mother liquor (total yield 74.7%). The methyl ester of 3-bromo-N-(phenylacetyl)-alanine is readily soluble in alcohol, less readily in ether. It can be recrystallized from water if heating is done cautiously.

Found %: C 48.28; H 4.74; Br 26.00; N 4.98
$C_{12}H_{14}O_3NBr$. Calculated %: C 48.01; H 4.70; Br 26.66; N 4.67

Acid Hydrolysis of 3-Bromo-N-(phenylacetyl)alanine (Preparation of Serine). A suspension of 50 g of 3-bromo-N-(phenylacetyl)alanine in 300 ml of water containing 1 ml of 40% HBr was heated under reflux; it was first heated on a water bath until the acid dissolved, and was then boiled for three hours. The solution was cooled, and the precipitated phenylacetic acid was filtered off; the filtrate was extracted three times with ether to remove phenylacetic acid completely. The aqueous solution was evaporated to dryness under reduced pressure. The residue was dissolved in 60 ml of 80% ethanol, and concentrated aqueous ammonia was added, with cooling, until the odor persisted. The mixture was left overnight in a refrigerator, and on the next day the precipitate was filtered off, washed with absolute alcohol, and dried. The product was 17 g of serine, m.p. 180 – 190°. Recrystallization from water yielded 13.1 g of serine, m.p. 230° (dec.). By addition of alcohol to the mother liquor, a further 1.4 g of serine was obtained. The total yield was 78.5%.

Found %: C 33.51; H 6.59; N 13.47
$C_3H_7O_3N$. Calculated %: C 34.28; H 6.71; N 13.39

The serine that we prepared was identified by means of chromatography on paper with serine prepared by another method. The hydrochloride of the methyl ester of serine and 3-chloroalanine were prepared from the serine and found to have melting points identical with those reported in the literature [3].

2-Benzylidene-4-methyl-3-oxazolin-5-one. A mixture of 0.8 g of 3-bromo-N-(phenylacetyl)alanine and 6 ml of acetic anhydride was warmed carefully until the acid dissolved, and acetic anhydride was then distilled off rapidly under reduced pressure. The residue was treated several times with absolute ether. The ether extract was filtered, and the ether was removed under reduced pressure. The residue was recrystallized from methanol and yielded 2-benzylidene-4-methyl-3-oxazolin-5-one in the form of light-yellow crystals melting at 129-131° [8]. The substance has an irritating effect on the eyes and mucous membrane.

S-Alkylation of Cysteine with 3-Bromo-N-(phenylacetyl)alanine. To a solution of 0.12 g (0.001 mole) of cysteine in 2 ml of NaOH (0.002 mole), 0.26 g (0.001 mole) of 3-bromo-N-(phenylacetyl)alanine was added. The solution was maintained alkaline by dropwise addition of 1 ml of N NaOH, and the mixture was set aside at room temperature overnight. On the next day the solution was evaporated to dryness at 50-60° under reduced pressure, and 4 ml of 20% hydrochloric acid was added to the residue. The mixture was refluxed for three hours, and the precipitated phenylacetic acid was filtered off. The filtrate was extracted three times with ether to remove residual phenylacetic acid. The aqueous solution was evaporated to dryness under reduced pressure, and the residue was dissolved in 1 ml of water. Saturated sodium acetate solution (1 ml) was added, and the precipitate formed was filtered off. The product was 0.1 g (50%) of lanthionine, melting with decomposition at 240°.

The lanthionine was purified for the analysis by reprecipitation from hydrochloric acid solution with saturated sodium acetate solution.

Found %: C 33.27; H 5.98; S 14.84
$C_6H_{12}O_4N_2S$. Calculated %: C 34.60; H 5.8; S 15.40

The substance was identical in properties with a sample of lanthionine specially prepared by Schoberl's method [12].

Reaction of 3,3-Dimethylcysteine with 3-Bromo-N-(phenylacetyl)alanine. To a solution of 0.6 g (0.004 mole) of 3,3-dimethylcysteine in 8 ml of N NaOH (0.008 mole), 1.15 g (0.004 mole) of 3-bromo-N-(phenylacetyl)-alanine was added. The solution was maintained alkaline by gradual addition of N NaOH (2 ml). The reaction mixture was set aside at room temperature overnight. On the next day there was still a feeble reaction for the mercapto group. The solution was acidified to pH 3.5-4 with 2 N HCl, and the oil formed was separated. When this oil was treated with 2 N HCl, part of it dissolved, and addition of a saturated sodium bicarbonate solution to the resulting solution until the pH was 3.5-4 yielded 2-benzyl-5,5-dimethyl-2-thiazoline-4-carboxylic acid, m.p. 141-143°.

Found %: C 62.44; H 6.16; S 12.56; N 5.5
$C_{13}H_{15}O_2NS$. Calculated %: C 62.62; H 6.06; S 12.86; N 5.62

The residue, insoluble in hydrochloric acid, was recrystallized from water. The product was 3,3-dimethyl-N-(phenylacetyl)cysteine, m.p. 129-130°, undepressed by admixture of known 3,3-dimethyl-N-(phenylacetyl)-cysteine.

The solution remaining after separation of the oil was evaporated to dryness under reduced pressure, and the residue was dissolved in absolute alcohol. Ammonia was added to the alcoholic solution until the odor persisted, and the mixture was set aside in a refrigerator overnight. The precipitate formed was recrystallized from water, and it then melted with decomposition at 220°. It gave a positive ninhydrin test for α-amino acids; it did not contain sulfur; it had a sweet taste. In admixture with serine it showed no melting point depression.

N-Benzoyl-3-bromoalanine. Dry hydrogen bromide (dried over phosphoric oxide) was passed into a suspension of 2 g (0.01 mole) of 2-benzamidoacrylic acid in 4 ml of glacial acetic acid (distilled over phosphoric oxide). After ten minutes the whole of the acid had dissolved. When HBr ceased to be absorbed (one hour), the solution was poured into 12 ml of ice water. The oil that separated solidified and it was filtered off and washed with cold water until it ceased to be acid to Congo red. The product was 1.9 g (66%) of N-benzoyl-3-bromoalanine, which melted with decomposition at 136-137° after recrystallization from ethyl acetate. The acid is readily soluble in alcohol and acetone, and it can be recrystallized from ether. An exactly weighed sample of the acid was boiled with 0.1 N NaOH for 20 minutes, and the solution was acidified with nitric acid and titrated by Volhard's method:

Found %: Br 29.2
$C_{10}H_{10}O_3NBr$. Calculated %: Br 29.4

With diazomethane N-benzoyl-3-bromoalanine yielded its methyl ester, m.p. 116-117° (the literature [6] gives 115-117°).

O-Benzoylserine. A mixture of 2.7 g of N-benzoyl-3-bromoalanine, 15 ml of water, and 2-3 drops of 40% HCl was heated under reflux until the acid dissolved, and then boiled for two hours. The solution was evaporated to one-fifth bulk under reduced pressure, and was extracted with ether. Concentrated ammonia was added to the aqueous solution until the odor persisted, and the mixture was set aside in a refrigerator for four hours. The finely-crystalline precipitate was filtered off. The product was O-benzoylserine, m.p. 150°; the O-benzoylserine prepared by Fry [5] by the hydrolysis of 2-phenyl-2-oxazoline-4-carboxylic acid also melted at 150°. O-Benzoylserine gives a positive ninhydrin test for α-amino acid. A further 0.5 g of O-benzoylserine was obtained from the mother liquor. The total yield was 75%.

Found %: C 57.07; H 4.99
$C_{10}H_{11}O_4N$. Calculated %: C 57.41; H 5.30

In order to obtain serine, N-benzoyl-3-bromoalanine must be boiled for two hours with 20% hydrochloric acid.

N-Benzoyl-3-chloroalanine*. Dry hydrogen chloride was passed for one hour into a solution of 5 g of 2-benzamidoacrylic acid in 25 ml of dry dioxane. Dioxane was removed under reduced pressure, and 10 ml of ice water was added to the residue. The precipitate was filtered off, washed with ice water until no longer acid to Congo red, and dried. The product was 3.3 g of N-benzoyl-3-chloroalanine, m.p. 143-144° (after being washed with warm benzene and chloroform). Fry [6] gives a value of 145-147° for the melting point of N-benzoyl-3-chloroalanine.

Found %: C 53.41; H 4.52; Cl 14.26

$C_{10}H_{10}O_3NCl$. Calculated %: C 52,76; H 4.43; Cl 15.58

3-Chloro-N-(phenylacetyl)alanine*. Treatment of 2-(2-phenylacetamido)acrylic acid by the same method yielded 3-chloro-N-(phenylacetyl)alanine, m.p. 174-175° (from ethyl acetate).

Found %: C 54.43; H 5.15; Cl 14.73

$C_{11}H_{12}O_3NCl$. Calculated %: C 54.66; H 5.01; Cl 14.67

Phenaceturic Anhydride. A mixture of 10 g of phenaceturic acid and 30 ml of acetic anhydride was heated for 5-10 minutes at 60° at a residual pressure of 40 mm; the whole of the acid dissolved. The temperature was lowered to 30-40° and acetic anhydride was distilled off under reduced pressure until crystallization began. The crystals were filtered off, washed with ether, with sodium bicarbonate solution, and with water, and dried over phosphoric oxide in a desiccator. The product was 6 g (64.5%) of phenaceturic anhydride, m.p. 115-117°. Strukov has prepared phenaceturic anhydride, for which he gives the melting point 108-109° [13].

3,3-Dimethyl-N-phenaceturylcysteine. Phenaceturic anhydride (1.84 g, i.e. 0.005 mole) was added at 10° to 0.73 g (0.005 mole) of 3,3-dimethylcysteine in 5 ml of water containing 0.4 g (0.01 mole) of sodium hydroxide, and the mixture was shaken until the anhydride dissolved (5-10 minutes). The solution was acidified to Congo red with 2 N HCl, and the precipitate that formed, which consisted of a mixture of 3,3-dimethyl-N-phenaceturylcysteine and phenaceturic acid, was repeatedly crystallized from hot water (the temperature of the water was not above 70°). The product was 0,8 g (50%) of 3,3-dimethyl-N-phenaceturylcysteine, m.p. 142-144°.

Found %: C 55,63; H 6,19; S 9.95

$C_{15}H_{20}O_4N_2S$. Calculated %: C 55,53; H 6,21; S 9.88

S-(Carboxymethyl)-3,3-dimethyl-N-phenaceturylcysteine. Chloroacetic acid (0.4 g, i.e. 0.004 mole) was added at 0° to 0.65 g (0.002 mole) of 3,3-dimethyl-N-phenaceturylcysteine in 2 ml of 2 N NaOH, and 2 N NaOH was added until the mixture was alkaline to phenolphthalein. After one hour positive tests for the SH group were no longer obtained. The solution was cooled with ice and acidified to Congo red with concentrated hydrochloric acid. The oil that separated solidified when rubbed out with ether. After purification by reprecipitation with ether from alcoholic solution, the S-(carboxymethyl)-3,3-dimethyl-N-phenaceturylcysteine melted at 90-100° with decomposition.

Found %: C 53,65; H 5.97; N 7.66

$C_{17}H_{22}O_6N_2S$. Calculated %: C 53.38; H 5.80; N 7.32

4-Benzamido-4-methyl-2-phenyl-2-oxazolin-5-one. This substance was prepared by Nicolet's method [10] by the action of acetic anhydride on 2,2-dibenzamidopropionic acid. After being recrystallized from benzene it melted at 193°.

Methyl 2,2-Dibenzamidopropionate. Treatment of 4-benzamido-4-methyl-2-phenyl-2-oxazolin-5-one with methanol containing traces of HCl resulted in the formation of methyl 2,2-dibenzamidopropionate, m.p. 167-168°. A mixture test with the ester obtained by treating 2,2-dibenzamidopropionic acid with diazomethane showed no depression.

Hydrochloride of 4-Benzamido-4-methyl-2-phenyl-2-oxazolin-5-one. Freshly distilled thionyl chloride (3 g) was poured onto 1.5 g of 2,2-dibenzamidopropionic acid. In the course of 30 minutes the whole of the acid dissolved and a new crystalline precipitate formed. The reaction mixture was heated under reflux in a water bath until bubbles of gas ceased to be evolved. Excess of thionyl chloride was removed under reduced pressure. The residue was washed with absolute ether. The product was 1.4 g of the hydrochloride of 4-benzamido-4-methyl-2-phenyl-2-oxazolin-5-one, melting with decomposition at 160°. An exactly weighed sample of the oxazolinone hydrochloride was shaken with water, nitric acid was added, and ionic chlorine was titrated by Volhard.

---

* A. I. Guseva aided in the preparation of N-benzoyl-3-chloro- and 3-chloro-N-(phenylacetyl)-alanines.

Found %: Cl 10.60

$C_{17}H_{15}O_3N_2Cl$. Calculated %: Cl 10.72

When the oxazolinone hydrochloride was boiled with 2 molecular proportions of 0.1 N NaOH and the solution acidified, the original 2,2-dibenzamidopropionic acid was recovered.

N-(2,2-Dibenzamidopropionyl)-3,3-dimethylcysteine. To a solution of 0.5 g (0.0033 mole) of 3,3-dimethylcysteine in 13 ml of 0.5 N NaOH (0.0066 mole) 1 g (0.0033 mole) of 4-benzamido-4-methyl-2-phenyl-2-oxazolin-5-one was added. The reaction mixture was maintained at 50° for three hours, in the course of which almost the whole of the oxazolinone went into solution. The solution was filtered and acidified to Congo red with N HCl. The precipitate that formed was filtered off, washed with water, and dried. The product was 0.75 g (50%) of N-(2,2-dibenzamidopropionyl)-3,3-dimethylcysteine, m.p. 203-204°. The substance was purified by reprecipitation from alcoholic solution with water.

Found %: C 59.30; H 5.54; S 6.86

$C_{22}H_{25}O_5N_3S$. Calculated %: C 59.57; H 5.68; S 7.23

N-(2,2-Dibenzamidopropionyl)-3,3-dimethylcysteine is readily soluble in ethyl, methyl, and butyl alcohols, and in chloroform, ethyl acetate, and dioxane; it is insoluble in water and ether.

2-Benzyl-4-methyl-4-(2-phenylacetamido)-2-oxazolin-5-one (Oxazolinone derived from 2,2-Bis(2-phenylacetamido)propionic Acid). A mixture of 3.4 g (0.1 mole) of 2,2-bis (2-phenylacetamido)propionic acid and 12 ml of acetic anhydride was heated in a water bath until the acid had completely dissolved (two hours). The mixture was then cooled to room temperature and practically the whole of it solidified. The precipitate was filtered off, washed with sodium bicarbonate solution and with water, and dried. The product was 2.3 g (70%) of the oxazolinone, m.p. 169-170° (from absolute ethyl acetate).

Found %: C 71.21; H 5.76

$C_{19}H_{18}O_3N_2$. Calculated %: C 70.79; H 5.95

N-[2,2-Bis(2-phenylacetamido)propionyl]-3,3-dimethylcysteine. 2-Benzyl-4-methy-4-(2-phenylacetamido)-2-oxazolin-5-one (0.65 g, i.e. 0.002 mole) was added to 0.3 g (0.002 mole) of 3,3-dimethylcysteine in 4 ml of N NaOH (0.004 mole), and the mixture was maintained at 50° until the oxazolinone had dissolved completely (30 minutes). The solution was filtered and acidified to Congo red with N HCl. The precipitate formed was filtered off, washed with water, and dried. The product was 0.37 g (40%) of N-[2,2-bis(2-phenylacetamido)-propionyl]-3,3-dimethylcysteine, melting at 187-189° after three crystallizations form 50% alcohol.

Found %: C 61.25; H 6.08; S 6.58

$C_{24}H_{29}O_5N_3S$. Calculated %: C 61.12; H 6.20; S 6.80

SUMMARY

1. α-Acylamino β-halo acids were prepared by addition of hydrogen bromide and hydrogen chloride to 2-(acylamino)acrylic acids. Serine was prepared in almost quantitative yield by the hydrolysis of 3-bromo-N-(phenylacetyl)alanine.

2. It was shown that 3,3-dimethylcysteine is readily acylated under normal conditions by oxazolinones and anhydrides of acylamino carboxylic acids with formation of N-acyl derivatives, for example, 3,3-dimethyl-N-phenaceturylcysteine and N-(2,2-dibenzamidopropionyl)-3,3-dimethylcysteine.

3. The reaction of 3,3-dimethylcysteine with 3-bromo-N-(phenylacetyl)alanine in aqueous medium is accompanied by intermolecular transacylation with formation of 3,3-dimethyl-N-(phenylacetyl)cysteine and 2-benzyl-5,5-dimethyl-2-thiazoline-4-carboxylic acid.

LITERATURE CITED

[1] I. L. Knunyants and M. G. Linkova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 1, 62. *

[2] E. Rotstein, J. Chem. Soc. 1949, 1968.

[3] E. P. Pointer, J. Am. Chem. Soc., 69, 229 (1947).

---

* Consultant's Bureau Translation, p 53.

[4] M. Bergmann, K. Grafe, Z. physiol. Chem. 187, 197 (1930).

[5] E. Fry, J. org. Chem. 14, 887 (1949).

[6] E. Fry J. org. Chem. 15, 438 (1950).

[7] O. V. Kildisheva, M. G. Linkova, and I. L. Knunyants, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 2, 271.*

[8] Chemistry of Penicillin, Princeton Univ. Press, 1949, 794, 798.

[9] O. Süs, Ann. 561, 31 (1948).

[10] B. Nicolet, J. Am. Chem. Soc. 57, 1073 (1935).

[11] M. Brenner, K. Rüfenacht, Helv. 36, 1832 (1953).

[12] A. Schoberl, A. Wagner, Ber. 80, 379 (1947).

[13] I. T. Strukov, J. Gen. Chem. 23, 438 (1953).**

Received April 9, 1954

N. D. Zelinsky Institute of Organic Chemistry of
the USSR Academy of Sciences

---

* Consultant's Bureau Translation, p 241

** Consultant's Bureau Translation, p 449

NEW METHOD FOR THE PREPARATION OF PRIMARY AND SECONDARY ORGANOARSENIC COMPOUNDS

I. L. Knunyants and V. Ya. Pilskaya

Among the numerous methods for the preparation of organoarsenic compounds, the most important are those yielding alkyl- and aryl-arsonic acids. The most noteworthy of these methods are those due to Meyer [1] and to Burt [2]. From the preparative point of view, Meyer's method has been found very convenient for various alkylarsonic acids, but some of these arsonic acids are obtained in very low yield, the yields of butyl- and isopentyl arsonic acids, for example, being only 5-10% [3].

The yield obtained in Meyer's reaction depends on the reactivity of the alkyl halide. Whereas benzyl and allyl bromide, and 2-chloroethanol react with an arsenite at a high rate, ethyl bromide, and particularly isopropyl bromide, phenoxypropyl bromide, and ethylene dibromide, react very slowly with sodium arsenite, and practically no arsonic acid is formed [3]. Phenethyl bromide does not react with sodium arsenite, neither under the usual conditions, nor at 180° in presence of copper [4], and styryl bromide, in reacting with sodium arsenite, forms styrylarsonic acid in only very low yield.

It is known that aryl halides react with alkali-metal arsenites only under special conditions. The same applies to halogen derivatives of thiophene and furan [5]. Secondary alkyl halides react with difficulty with arsenic trioxide, and the tertiary do not react at all [6].

Meyer's reaction, therefore, in spite of its simplicity and of the accessibility of the starting materials, has some limitations that restrict its applicability.

The present investigation is devoted to the development of a method for the preparation of organoarsenic compounds which will be convenient for the preparation of some difficultly accessible compounds. The method consists in the preparation of alkyl- and aryl-(2-chlorovinyl)arsines, followed by elimination of the 2-chlorovinyl group. The possibility of such elimination is based on the tendency of 2-chlorovinylarsenic compounds to undergo cleavage under the action of alkalis. Such compounds include, in particular, dichloro(2-chlorovinyl)arsine and chlorobis(2-chlorovinyl)arsine.

It is known that the stereoisomeric dichloro(2-chlorovinyl)arsines behave differently toward alkalis. Whereas the trans isomer yields acetylene quantitatively when treated with a 15% solution of caustic alkali in the cold, cis-dichloro(2-chlorovinyl)arsine, treated in a similar way, yields only disodium 2-chlorovinyl arsenite, which will then give vinyl chloride when heated with alkali to 40-80° [7]. Dichloro(2-chlorovinyl)- and chlorobis(2-chlorovinyl)-arsines, being acid chlorides containing very mobile chlorine atoms, readily react with organomagnesium compounds, and as a result alkyl- and aryl-bis(2-chlorovinyl)arsines and dialkyl- and diaryl-(2-chlorovinyl)arsines are obtained [8, 9]. The resulting tertiary alkyl- and aryl-(2-chlorovinyl)arsines should retain the characteristic properties of 2-chlorovinyl compounds. Since there is about 90% of the trans form in technical dichloro(2-chlorovinyl)arsine [7], the trans configuration of the 2-chlorovinyl group should predominate also in tertiary alkyl- and aryl-(2-chlorovinyl)arsines obtained from lewisite and confer the characteristic property of acetylene evolution under the action of alkaline reagents.

The method that we have developed consists essentially in the reaction of alkylmagnesium halide with chlorobis(2-chlorovinyl)arsine or dichloro(2-chlorovinyl)arsine to yield tertiary arsines:

$$RMgX + ClAs(CH{=}CHCl)_2 \rightarrow RAs(CH{=}CHCl)_2 + MgXCl$$

or

$$2RMgX + Cl_2AsCH{=}CHCl \rightarrow R_2AsCH{=}CHCl + 2MgXCl$$

The resulting tertiary (2-chlorovinyl)arsine is decomposed with aqueous or alcoholic alkali:

$$RAs(CH{=}CHCl)_2 + 2NaOH \rightarrow RAsO + 2C_2H_2 + 2NaCl + H_2O$$

or

$$2R_2AsCH{=}CHCl + 2NaOH \rightarrow [R_2As]_2O + 2C_2H_2 + 2NaCl + H_2O.$$

This method was verified for methyl iodide, ethyl bromide, propyl bromide, isopropyl bromide, butyl bromide, butyl iodide, isopentyl bromide, bromobenzene, p-bromotoluene, cyclohexyl bromide, and styryl bromide.

These alkyl halides were treated with magnesium in dry ether in order to obtain the corresponding alkylmagnesium halides which were then caused to react with chlorobis(2-chlorovinyl)arsine, when they yielded a series of alkyl- and aryl-bis (2-chlorovinyl)arsines (Table 1).

TABLE 1

Alkyl or aryl halide	Tertiary arsine	B.p. in °C (p in mm)	Yield (%)
CH_3I	$CH_3As(CH = CHCl)_2$	142 (10)	
C_2H_5Br	$C_2H_5As(CH = CHCl)_2$	100 (6)	
$n\text{-}C_3H_7Br$	$n\text{-}C_3H_7As(CH = CHCl)_2$*	112 (4)	89.4
$i\text{-}C_3H_7Br$	$i\text{-}C_3H_7As(CH = CHCl)_2$*	115 (10)	79.8
$n\text{-}C_4H_9Br$	$n\text{-}C_4H_9As$ $CH = CHCl)_2$*	106 (8)	89.3
$i\text{-}C_5H_{11}Br$	$i\text{-}C_5H_{11}As(CH = CHCl)_2$*	126 (3)	87.5
C_6H_5Br	$C_6H_5As(CH = CHCl)_2$	170 (5)	
$p\text{-}CH_3C_6H_4Br$	$p\text{-}CH_3C_6H_4As(CH = CHCl)_2$*	165 (3)	78.3
$cyclo\text{-}C_6H_{11}Br$	$cyclo\text{-}C_6H_{11}As(CH = CHCl)_2$*	148 (10)	73.3
$C_6H_5CH = CHBr$	$C_6H_5CH = CHAs(CH = CHCl)_2$*	125 (3)	44

---

* Compounds not described previously.

Reaction of alkylmagnesium halides with dichloro(2-chlorovinyl)arsine yielded the tertiary arsines listed in Table 2.

TABLE 2

Alkyl or aryl halide	Tertiary arsine	B.p. in °C (p in mm)	Yield (%)
CH_3I	$(CH_3)_2As-CH = CHCl$*	42 (13)	51
C_2H_5Br	$(C_2H_5)_2AsCH = CHCl$*	66 (7)	69.6
$i\text{-}C_3H_7Br$	$(i\text{-}C_3H_7)_2As-CH = CHCl$*	90 (6)	47
$n\text{-}C_4H_9Br$	$(n\text{-}C_4H_9)_2As-CH = CHCl$*	110 (3)	67
$i\text{-}C_5H_{11}Br$	$(i\text{-}C_5H_{11})_2As-CH = CHCl$*	123 (3)	66.5
C_6H_5Br	$(C_6H_5)_2As-CH = CHCl$*	176 (3)	57
$n\text{-}CH_3C_6H_4Br$	$(n\text{-}CH_3C_6H_4)_2As-CH = CHCl$*	197 (3)	59.5

---

* Compounds not described previously

In these reactions tertiary arsines are formed in high yields. It must be pointed out that, in the decomposition of alkyl- and aryl-(2-chlorovinyl)arsines, the yield of acetylene is not 100%. The fact that acetylene is eliminated in an amount approximating to 90% of the theoretical yield indicates that about 90% of the tertiary arsine has 2-chlorovinyl groups in the trans configuration. The conversion of the organoarsenic oxides, formed as a result of the alkaline decomposition of alkyl(2-chlorovinyl)arsines, into haloarsines presents no difficulty.

TABLE 3

Haloarsine	Yield (%)		
	Meyer's method	Cleavage of 10-alkyl-5,10 dihydrophenarsazine with hydrochloric acid.	Proposed method
CH_3AsCl_2	78*	67	64.4
$C_2H_5AsCl_2$	77*	65	57.2
$n\text{-}C_3H_7AsCl_2$	65*	64	74.1
$i\text{-}C_3H_7AsCl_2$	0	67	58.1
$n\text{-}C_4H_9AsCl_2$	10*	52	84.9
$i\text{-}C_5H_{11}AsCl_2$	5-10*	51	74.6
$C_6H_5AsCl_2$	–		79.4
$p\text{-}CH_3C_6H_4AsCl_2$	–		92.2
$C_6H_5CH{=}CHAsCl_2$	0		41.8
$(CH_3)_2AsCl$		–	59.2
$(C_6H_5)_2AsCl$		–	52.8
$(i\text{-}C_5H_{11})_2AsCl$	0	–	44.4

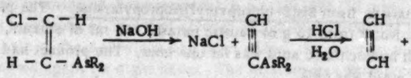
Table 3 gives the yields of the corresponding haloarsines, as prepared by Meyer's method, by the cleavage of 10-alkyl-5, 10-dihydrophenarsazine with hydrochloric acid (Zeide's method), and by the new method that we have proposed.

---

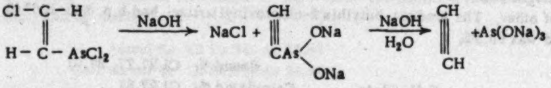
* This column gives the yield of arsonic acid, not haloarsine.

An analysis of the data in Table 3 shows that the proposed method has advantages over Meyer's method in the preparations of dichloroisopropylarsine, butyldichloroarsine, dichloroisopentylarsine, dichlorostyrylarsine, and chlorodiisopentylarsine. The proposed method has preparative advantages over Zeide's method, and in addition it makes it possible to prepare secondary organoarsenic oxides also.

An unequivocal interpretation of the mechanism of the decomposition of 2-chlorovinyl organometallic compounds has not yet been given [11, 12]. The most probable scheme for the decomposition is elimination of HCl from alkyl(2-chlorovinyl)arsines with formation of alkylethynylarsines, and the decomposition of these by water or hydrochloric acid to yield acetylene and the corresponding haloarsine (or organoarsenic oxide):



It must be supposed that the cleavage of trans-dichloro(2-chlorovinyl)arsine (α-lewisite) will proceed according to a similar scheme:



Indirect confirmation of the formation of alkylethynylarsines is provided by experiments that we have carried out on the decomposition of the above-mentioned tertiary arsines with sodium ethoxide and with amines at room temperature. As objects for investigation (2-chlorovinyl)diethylarsine and dibutyl(2-chlorovinyl)arsine were taken. When dibutyl(2-chlorovinyl)arsine was treated with piperidine for four hours at room temperature, 20% of the theoretical amount of piperidine hydrochloride was isolated, and in the decomposition of (2-chlorovinyl)diethylarsine with alcoholic alkali 24.9% of the theoretical amount of sodium chloride was obtained; in both experiments the yield of acetylene was only 1%. The noncorrespondence between the amount of piperidine hydrochloride or sodium chloride isolated and the amount of acetylene obtained may be regarded as evidence of the formation of alkylethynylarsines.

EXPERIMENTAL

Preparation of Starting Materials. Tertiary alkyl- and aryl-arsines of the type $RAs(CH = CHCl)_2$ were prepared from the corresponding alkyl- and aryl-magnesium halides and freshly distilled chlorobis(2-chlorovinyl)arsine, b.p. 101-102° (3 mm); d_4^{20} 1.7018; n_D^{20} 1.6088. Tertiary arsines of the type $R_2AsCH = CHCl$ were prepared from freshly distilled dichloro(2-chlorovinyl)arsine, b.p. 71-72° (3 mm); d_4^{20} 1.8879; n_D^{20} 1.6108.

1. Preparation of Bis(2-chlorovinyl)propylarsine. A solution of 47 g of chlorobis(2-chlorovinyl)arsine in 250 ml of dry ether was added dropwise with vigorous stirring and ice-cooling to a Grignard reagent prepared from 8 g of magnesium turnings and 43 g of propyl iodide in 100 ml of dry ether. The reaction mixture was then heated in a water bath for one hour. It was then cooled and poured carefully into ice water containing some hydrochloric acid. The ether layer was separated and washed three times with ice water; the aqueous layer was extracted with ether. The ether extracts were united and dried with sodium sulfate. The ether was distilled off, and the oil that remained was vacuum-distilled, when it yielded a clear colorless liquid, b.p. 112° (4 mm); d_4^{20} 1.4174; n_D^{20} 1.5522; yield 43 g (89%).

Found %: Cl 29.33; As 30.84
$C_7H_{11}Cl_2As$. Calculated %: Cl 29.43; As 31.11

2. Conversion of Bis(2-chlorovinyl)propylarsine into Dichloropropylarsine. Dry caustic potash powder (13 g) and ethanol (100 ml) were placed in a round-bottomed flask fitted with reflux condenser connected to a calibrated gas holder. Bis(2-chlorovinyl)propylarsine (b.p. 112°/4 mm) (24 g) was added gradually from a dropping funnel. When acetylene ceased to be evolved (3.5 liters, i.e. 78% of the theoretical amount, was obtained), alcohol was distilled from the reaction mixture, and dichloropropylarsine was isolated from the dry residue. For this purpose excess of hydrochloric acid was added carefully to the dry residue, and the mixture was refluxed in a stream of hydrogen chloride for one hour. The oil that separated was extracted with chloroform, the chloroform solution was dried with sodium sulfate, the chloroform was distilled off, and the oil that remained was vacuum-distilled.

The distillation yielded 14 g (74.1%) of a clear colorless liquid having a sharp unpleasant odor; b.p. 90-93° (46-52 mm); d_{20}^{20} 1.5123; n_D^{20} 1.5358.

3. Bis(2-chlorovinyl)isopropylarsine. This substance was prepared under the conditions of Expt. No. 1 from 8 g of magnesium, 49.7 g of isopropyl bromide, 100 ml of ether and 58 g of chlorobis(2-chlorovinyl)arsine. The substance boiled at 115° (10 mm). The yield was 80%.

Found %: Cl 29.39; As 30.89

$C_7H_{11}Cl_2As$. Calculated %: Cl 29.43; As 31.11

4. Dichloroisopropylarsine from Bis(2-chlorovinyl)isopropylarsine. The preparation was carried out under the conditions of Expt. No. 2 from 15 g of caustic potash, 100 ml of ethanol, and 24 g of bis(2-chlorovinyl)-isopropylarsine. Boiling with hydrochloric acid was for one hour. The product had b.p. 64-66° (12-13 mm); d_4^{20} 1.5722; n_D^{20} 1.5289; The yield was 58%.

5. Butylbis(2-chlorovinyl)arsine. This substance was prepared under the conditions of Expt. No. 1 from 17 g of magnesium, 126 g of butyl iodide, 100 ml of ether, and 116.7 g of chlorobis(2-chlorovinyl)arsine in 250 ml of ether. The product, butylbis(2-chlorovinyl)arsine, had b.p. 105-106° (8 mm); d_4^{20} 1.3660; n_D^{20} 1.5488. The yield was 89.3%.

Found %: Cl 27.77; 27.61

$C_8H_{13}Cl_2As$. Calculated %: Cl 27.81

6. Butyldichloroarsine. Butylbis(2-chlorovinyl)arsine (12.8 g) was decomposed in the usual way with alcoholic alkali, and 2 liters (92% of the theoretical amount) of acetylene was collected. Alcohol was distilled off, and excess of hydrochloric acid was added to the dry residue. The mixture was refluxed in a stream of hydrogen chloride for one hour. The oil that separated was extracted with chloroform. Chloroform was distilled off, and vacuum distillation of the oil yielded 8.6 g (89.9%) of a colorless liquid, b.p. 58-60° (5 mm), n_D^{20} 1.5238. Oxidation of a 0.5-g sample of the butyldichloroarsine with hydrogen peroxide yielded 0.4 g (89.2%) of butylarsonic acid, m.p. 158-159°, in the form of white crystals.

7. Bis(2-chlorovinyl)isopentylarsine. This substance was prepared under the conditions of Expt. No. 1 from 12 g of magnesium, 76 g of isopentyl bromide in 100 ml of dry ether, and 58 g of chlorobis(2-chlorovinyl)-arsine in 200 ml of ether. Bis(2-chlorovinyl)isopentylarsine is a clear colorless liquid, b.p. 125-126° (3 mm); d_4^{20} 1.2859; n_D^{20} 1.5390; The yield was 87.5%.

Found %: Cl 26.36; As 27.94

$C_9H_{15}ClAs$. Calculated %: Cl 26.39; As 27.88

8. Dichloroisopentylarsine from Bis (2-chlorovinyl)isopentylarsine. Bis (2-chlorovinyl)isopentylarsine (26 g) was added dropwise to 14 g of caustic potash powder in 100 ml of ethanol. The reaction mixture was heated in a water bath, and the gas evolved was collected in a graduated gas holder (4.2 liters, i.e. 94% of the theoretical amount, of gas was collected). From 50 ml of the gas the Ilosvay reagent absorbed 44 ml, corresponding to an acetylene content of 99%. Alcohol was distilled from the reaction mixture, excess of hydrochloric acid was added carefully to the dry residue, and the mixture was heated under reflux in a stream of hydrogen chloride for one hour. The oil that separated was filtered from the precipitate and extracted with chloroform. The chloroform solution was dried with calcium chloride, and the residue after removal of chloroform was vacuum-distilled, when it yielded:

Frac. I, b.p. 91-92° (8 mm); 16.2g

Frac. II, b.p.100-130° (8 mm); 2.9 g (unchanged β-lewisite)

Fraction I, obtained in 74.6% yield, was a clear colorless liquid having a characteristic odor; d_4^{20} 1.3863; n_D^{20} 1.5170 . Oxidation of 1 g of the dichloroisopentylarsine with nitric acid yielded 0.5 g of isopentylarsonic acid in the form of scales melting at 194°.

9. Bis(2-chlorovinyl)-p-tolylarsine. This substance was prepared under the conditions of Expt. No. 1 from 9.6 g of magnesium, 42.7 g of p-bromotoluene, 150 ml of ether, and 49.6 g of chlorobis(2-chlorovinyl)-arsine in 200 ml of dry ether. Bis(2-chlorovinyl)-p-tolylarsine is a clear colorless liquid, b.p. 165-167° (3 mm); d_4^{20} 1.3676; n_D^{20} 1.5990. The yield was 78.3%.

Found %: Cl 24.97; As 25.71

$C_{11}H_{11}Cl_2As$. Calculated %: Cl 24.55; As 25.95

10. Dichloro-p-tolylarsine from Bis(2-chlorovinyl)-p-tolylarsine. Bis(2-chlorovinyl)-p-tolylarsine (20g) was decomposed by heating it with alcoholic caustic potash, when 2.8 liters (90%) of gas was evolved. Alcohol was distilled off, hydrochloric acid (excess) was added cautiously to the dry residue, and the mixture was boiled under reflux in a stream of hydrogen chloride. The oil that separated was extracted with chloroform, and the extract was dried with calcium chloride. After removal of chloroform, 15.1 g (92.7%) of slightly yellowish crystals remained. The melting point of the crude product was 36-37°, and after crystallization from alcohol it melted at 42-43°. Oxidation of 1 g of the product (dichloro-p-tolylarsine) with hydrogen peroxide yielded 0.9 g (98.7%) of p-tolylarsonic acid, m.p. 206.5-207.5°.

11. Bis(2-chlorovinyl)styrylarsine. A Grignard reagent was prepared in the usual way from 6 g of magnesium turnings and 45.6 g of styryl bromide (β-bromostyrene), b.p. 119-122° (35 mm), in 100 ml of dry ether. With vigorous stirring and cooling a solution of 38.9 g of chlorobis(2-chlorovinyl)arsine in 200 ml of dry ether was added dropwise. When the whole of the β-lewisite had been added, the reaction mixture was heated, then set aside overnight, and finally heated again for eight hours. The mixture was poured cautiously into a beaker of ice water to which a little hydrochloric acid had been added. The ether layer was washed three times with cold water, and the aqueous layer was extracted with ether. The ether extracts were united and dried with calcium chloride. The ether was distilled off, and vacuum distillation of the residue yielded 22 g (44%) of a clear colorless liquid, b.p. 125-135° (3 mm) and d_4^{20} 1.4183.

Found %: Cl 23.84; As 24.85
$C_{12}H_{11}Cl_2As$. Calculated %: Cl 23.67; As 24.91

12. Dichlorostyrylarsine. Bis(2-chlorovinyl)styrylarsine (20 g) was decomposed in the usual way with alcoholic alkali. In the course of the decomposition, 2.9 liters (90%) of acetylene was evolved. Alcohol was distilled off, excess of hydrochloric acid was added to the dry residue, and the mixture was refluxed for one hour. The oil that separated was extracted with chloroform, and the extract was dried with calcium chloride. The oil remaining after removal of chloroform was vacuum-distilled and yielded:

Frac. I, b.p. 50-100° (5 mm); 2.4 g
Frac. II, b.p. 108-110° (5 mm); 6.5 g; (yield 41.8%)
Residue 0.4 g

Found %: Cl 36.45; As 38.44
$C_8H_7Cl_2As$. Calculated %: Cl 36.56; As 38.65

Dichlorocyclohexylarsine, dichloromethylarsine, and dichloroethylarsine, which are listed in Table 3, were prepared in a similar way.

13. Decomposition of Bis(2-chlorovinyl)phenylarsine [9] with Alkali. A 30% aqueous solution of caustic soda (30 ml) was added dropwise to 8.7 g of bis(2-chlorovinyl)phenylarsine (b.p. 170-178°/5 mm). The reaction mixture was heated until acetylene ceased to be evolved (1.3 liters, i.e. 91.5% of the calculated amount, was evolved). Of 50 ml of the gas obtained, 42.5 ml was absorbed by Ilosvay's reagent, corresponding to an acetylene content of 85%.

14. Dichlorophenylarsine. When acetylene ceased to be evolved, 100 ml of concentrated hydrochloric acid was added to the reaction mixture, which was then refluxed for six hours. The dark-brown oil that separated was extracted with ether. After removal of ether vacuum distillation of the residue yielded 5.6 g (79.4%) of a colorless liquid, b.p. 100-102° (2 mm); d_4^{13} 1.6410; n_D^{13} 1.6292.

Oxidation of 1 g of dichlorophenylarsine with hydrogen peroxide yielded 0.65 g (71.7%) of pure phenylarsonic acid, m.p. 157.5° (from water). There was no depression in a mixture test with known phenylarsonic acid.

15. (2-Chlorovinyl)dimethylarsine. This substance was prepared under the conditions of Expt. No. 1 from 12 g of magnesium, 61 g of methyl iodide, 100 ml of dry ether, and 52 g of dichloro(2-chlorovinyl)arsine in 250 ml of ether. It is a clear colorless liquid having the characteristic odor of tertiary arsines; b.p. 42° (13 mm); d_4^{20} 1.3923; The yield was 51%.

Found %: Cl 21.10; As 44.61
C_4H_8ClAs. Calculated %: Cl 21.31; As 45.03

16. Decomposition of (2-Chlorovinyl)dimethylarsine with Alkali. (2-Chlorovinyl)dimethylarsine (20.6 g) was added dropwise to 11.2 g of finely ground caustic potash in 100 ml of ethanol, and the mixture was heated under reflux in a water bath. The gas liberated was collected in a graduated gas holder over saturated brine (2.8 liters of gas, i.e. 99.2%, was evolved). The liquid was filtered from the precipitated potassium chloride, which was then washed with alcohol. Alcohol was distilled off under reduced pressure, and the residual oily liquid of unpleasant odor came over at 118-120° in a stream of carbon dioxide. The yield was 12 g (59.2%);

d_4^{15} 1.4603.

Found %: As 65.82

$C_4H_{12}As_2O$. Calculated %: As 66.35

Of 50 ml of the gas collected in the gas holder, 44.2 ml was absorbed by Ilosvay's reagent, which corresponds to an acetylene content of 88.4%. Chlorodiethylarsine, chlorodiisopropylarsine, dibutylchloroarsine, and chlorodiisopentylarsine were prepared similarly.

17. (2-Chlorovinyl)diphenylarsine. This substance was prepared under the conditions of Expt. No. 1 from 12 g of magnesium, 80 g of bromobenzene, 150 ml of dry ether, and 51 g of dichloro(2-chlorovinyl)arsine in 200 ml of ether. It is a clear colorless liquid having the characteristic odor of tertiary arsines b.p. 176-178° (3 mm); d_4^{20} 1.3394; n_D^{20} 1 6280; The yield was 57%.

18. Chlorodiphenylarsine. 20.5 g of (2-chlorovinyl)diphenylarsine was decomposed with hot alcoholic alkali; ~~84.2% of the calculated amount~~ of acetylene was evolved. Alcohol was distilled from the reaction mixture. excess of hydrochloric acid added cautiously to the dry residue, and the mixture was refluxed for one hour in a stream of hydrogen chloride. The oil that separated was extracted with chloroform, and the extract dried with sodium sulfate. Chloroform was distilled off; vacuum-distillation of the residue gave the following fractions.

Found %: Cl 12.03; As 25.55

$C_{14}H_{12}ClAs$. Calculated %: Cl 12.21; As 25.81

The yield of the main fraction (II) was 62.8%. Fraction II was a clear colorless liquid (d_{40}^{40} 1.3522; n_D^{40} 1.6428) that rapidly solidified. After recrystallization from alcohol it had m.p. 37.8-38.3°. undepressed by admixture of known chlorodiphenylarsine.

Oxidation of 1 g of the chlorodiphenylarsine with hydrogen peroxide yielded 0.8 g (83%) of diphenylarsinic acid. m.p. 173-174°. undepressed by admixture of known diphenylarsinic acid. Chlorodi-p-tolylarsine was prepared similarly.

SUMMARY

1. A method was developed for the preparation of primary and secondary alkyl-and aryl-haloarsines; an alkyl- or aryl-(2-chlorovinyl)arsine is split by means of alkali, and the resulting organoarsenic oxide is then treated with hydrochloric acid. The method is general, and it makes it possible to prepare various haloarsines, including some that cannot be prepared by Meyer's reaction. In particular, dichloroisopropyl-, butyldichloro-, dichloroisopentyl-, and dichlorostyryl-arsines can be prepared in satisfactory yields.

2. It is probable that, in the decomposition of alkyl(2-chlorovinyl)arsines with alkalis, alkylethynylarsines are formed, and these then react with water with formation of acetylene and organoarsenic oxides.

Received May 20, 1954

LITERATURE CITED

[1] G. Meyer, Ber. 16, 1440 (1883).

[2] H. Burt, Ann. 423, 174 (1920).

[3] W. M. Dehn, Am. Chem. J. 35, 48 (1906).

[4] E. E. Turner, F. W. Bury, J. Chem. Soc. 1926, 1207, 1443.

[5] W. W. Beck, C. S. Hamilton, J. Am. Chem. Soc. 60, 620 (1938).

[6] C. K. Banks, J. F. Morgan, J. Am. Chem. Soc. 69, 927 (1947).

[7] C. H. Hewett, J. Chem. Soc., 1948, 1203.

[8] W. L. Lewis, H. W. Stiegler, J. Am. Chem. Soc. 47, 2546 (1925).

[9] Nirenda Nath Das Gupta, C. 1936, II, 3089.

[10] O. A. Zeide and I. S. Gorsky, J. Russ. Chem. Soc. 61, 1566 (1929).

[11] V. V. Nekrasov and A. S. Nekrasov, J. Russ. Chem. Soc. 61, 71(1929).

[12] R. Kh. Freidlina, E. I. Brainina, and A. N. Nesmeyanov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1945, No 6, 647.

SYNTHESIS OF STEROID COMPOUNDS AND RELATED SUBSTANCES

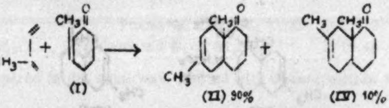
COMMUNICATION 29. CONDENSATION OF ISOPRENE WITH 2-METHYL-2-CYCLOHEXEN-1-ONE.

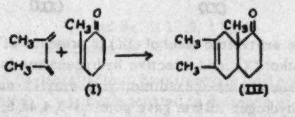
SYNTHESIS OF cis-1,2,4a,5,8,8a-HEXAHYDRO-4a,7-DIMETHYL-4-VINYLNAPHTHALENE

I. N. Nazarov and G. P. Kugatova

Various bicyclic dienes having angular methyl groups have been applied successfully in our laboratory in condensations with α,β-unsaturated cyclic ketones resulting in the synthesis of a variety of polycyclic compounds having cyclopentaphenanthrene and chrysene skeletons [1]. At the same time interesting observations were made on the spatial structure of the stereoisomeric tetracyclic ketones obtained in this way. However, for the detailed study of the stereochemistry of such compounds, more convenient model examples are provided by adducts formed by bicyclic dienes with such simple dienophiles as mesaconic ester and citraconic anhydride, such as were investigated in relation to the diene 1-vinylcyclohexene [2]. In this connection it was necessary to develop a method for the preparation of the most readily accessible bicyclic diene, and the present investigation was devoted to this problem.

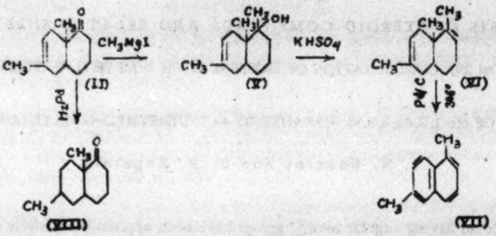
We selected cis-3,4,4a,5,8,8a-hexahydro-6,8a-dimethyl-1(2H)-naphthalenone (II) as the original bicyclic ketone containing an angular methyl group; it can be readily obtained by condensing isoprene with 2-methyl-2-cyclohexen-1-one (I) [3]. As a result of a series of experiments under various conditions (temperature, duration, ratio of components), it was shown that the condensation of isoprene with the methylcyclohexenone (I) goes best when the latter is in great excess and when heating is carried out in a nitrogen atmosphere for 45-50 minutes at 260-270°. Under these conditions, the yield of the adduct (II) (b.p. 92-93.5° at 2.5 mm; n^{20}_D 1.5015) was about 64%, based on the methylcyclohexenone that reacted. Under the same conditions cis-3,4,4a,5,8,8a-hexahydro-6,7,8a-trimethyl-1(2H)-naphthalenone (III) was obtained in 60% yield by the condensation of 2,3-dimethyl-1,3-butadiene with 2-methyl-2-cyclohexen-1-one (I):





It has been shown on the basis of numerous examples that various disubstituted dienes, such as isoprene [4], 2-phenyl-1,3-butadiene [5], and 2-methoxy-1,3-butadiene [6], when reacting with unsymmetrical dienophiles yield mixtures of adducts of para and meta structure in which the former predominates greatly. In most of these reactions the yield of meta isomer does not exceed 10-15%, so that its separation from the main product (the para form) is often very difficult.

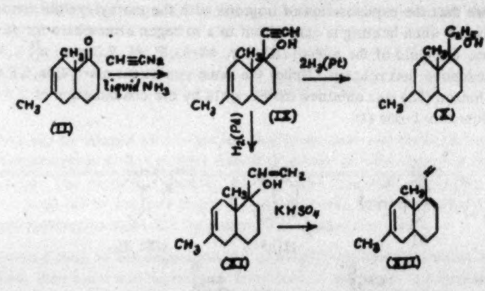
In order to prove the structure of the ketone (II), this was converted by reaction with methylmagnesium iodide into 1,2,3,4,4a,5,8,8a-octahydro-1,6,8a-trimethyl-1-naphthol (V), which was readily dehydrated with potassium hydrogen sulfate into the corresponding 3,4,4a,5,8,8a-hexahydro-1,6,8a-trimethylnaphthalene (VI) (or, with Chem. Abs. numbering, 1,2,4a,5,8,8a-hexahydro-4,4a,7-trimethylnaphthalene). Dehydrogenation of this substance in presence of palladized charcoal (5% Pd) at 350-360° for 36 hours gave a good yield of 1,6-dimethylnaphthalene (VII), identified as the picrate, m.p. 113-114°. These results show that our adduct consisted mainly of cis-3,4,4a,5,8,8a-hexahydro-6,8a-dimethyl-1(2H)-naphthalenone (II). Hydrogenation of the ketone (II) in presence of a palladium catalyst yielded cis-octahydro-6,8a-dimethyl-1(2H)-naphthalenone (VIII):



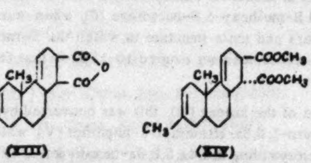
A more detailed investigation carried out in our laboratory has shown that the adduct formed by isoprene with 2-methyl-2-cyclohexeh-1-one (I) contains also about 10% of the isomeric cis-hexahydro-7,8a-dimethyl-1(2H)-naphthalenone (IV).

This fact, however, is of no real importance in the subsequent transformations, since it is found that it is then easy to isolate individual products corresponding to the main product (II).

For the preparation of the bicyclic diene from the ketone (II) we used a reaction that has been studied in detail in our laboratory, namely the condensation of cyclic dienes with acetylene in liquid ammonia, followed by partial hydrogenation and dehydration of the ethylenic alcohol [6]. When cis-3,4,4a,5,8,8a-hexahydro-6,8a-dimethyl-1(2H)-naphthalenone (II) was condensed with sodium acetylide in liquid ammonia, 1-ethynyl-1,2,3,4,4a,5,8,8a-octahydro-6,8a-dimethyl-1-vinyl-1-naphthol (IX) was obtained in a yield of about 90%:



Exhaustive hydrogenation of the acetylenic alcohol (IX) in presence of a platinum catalyst yielded 1-ethyldecahydro-6,8a-dimethyl-1-naphthol (X), and selective hydrogenation in presence of a palladium catalyst gave a good yield of 1,2,3,4,4a,5,8,8a-octahydro-6,8a-dimethyl-1-vinyl-1-naphthol (XI). Dehydration of the ethylenic alcohol (XI) with potassium hydrogen sulfate gave pure cis-3,4,4a,5,8,8a-hexahydro-6,8a-dimethyl-1-vinylnaphthalene (cis-1,2,4a,5,8,8a-hexahydro-4a,7-dimethyl-4-vinylnaphthalene) (XII) in a yield of about 70%.



The triene (XII) so obtained readily condenses with maleic anhydride and with dimethyl fumarate with formation of the corresponding adducts (XIII) and (XIV) in the form of liquid mixtures of stereoisomers. We intend to devote a special communication to the investigation of these adducts.

EXPERIMENTAL

cis-3,4,4a,5,8,8a-Hexahydro-6,8a-dimethyl-1(2H)-na=hthalenone (II). A mixture of 180 g of 2-methyl-

2-cyclohexen-1-one (I) (b.p. 55-55.5°/7 mm, n_D^{20} 1.4850 [3]) and 45 g of freshly distilled isoprene was heated at 270-280° for 45-50 minutes in a nitrogen atmosphere in a metal ampoule. Excess of methylcyclohexenone (145 g) was distilled off under reduced pressure. The condensation product from four similar experiments was combined and vacuum-distilled through a Vigreux column. The following fractions were obtained:

Frac. I, b.p. 54-74° (1 mm); n_D^{20} 1.4870; 12 g

Frac. II, b.p. 74-82° (1 mm); n_D^{20} 1.4890; 7.5 g

Frac. III, b.p. 82-84° (1 mm); n_D^{20} 1.5015; 52 g

Redistillation of Fraction III yielded 50 g of cis-3,4,4a,8,8a-hexahydro-6,8a-dimethyl-1(2H)-naphthalenone (II), b.p. 92-93.5; (2.5 mm); n_D^{20} 1.5015; d_4^{20} 0.9840; Calculated MR 52.76; Found MR 53.10.

Found %: C 80.79; 81.01; H 10.20; 10.20

$C_{12}H_{18}O$. Calculated %: C 80.89; H 10.11

The semicarbazone obtained from (II) in the usual way had a constant melting point of 219-220° (dec.) after recrystallization from methanol.

Found %: N 17.85

$C_{13}H_{21}ON_3$. Calculated %: N 17.86

The hexahydro-1(2H)-naphthalenone (II), which was found later to contain about 10% of the meta isomer (IV), was used in all of the reactions described below.

cis-3,4,4a,5,8,8a-Hexahydro-6,7,8a-trimethyl-1(2H)-naphthalenone (III). A mixture of 12 g of 2,3-dimethyl-1,3-butadiene [7] and 30 g of 2-methyl-2-cyclohexen-1-one (I) was heated for 35-40 minutes at 250-255° in a nitrogen atmosphere in a metal ampoule. The excess of methylcyclohexenone was distilled off. Residues from three similar experiments were distilled under reduced pressure and yielded:

Frac. I, b.p. 80-105° (2.5 mm); n_D^{20} 1.5001; 4.5 g

Frac. II, b.p. 105-107° (2.5 mm); n_D^{20} 1.5090; 13.4 g

Redistillation of Fraction II yielded 12.2 g of pure cis-3,4,4a,5,8,8a-hexahydro-6,7,8a-trimethyl-1(2H)-naphthalenone (III), b.p. 106-107.5° (2.5 mm) and n_D^{20} 1.5090.

Found %: C 81.34; 81.48; H 10.52; 10.44

$C_{13}H_{20}O$. Calculated %: C 81.20; H 10.40

The semicarbazone, prepared in the usual way, melted with decomposition at 240-241° after crystallization from butyl alcohol.

Found %: N 17.3; 17.15

$C_{14}H_{23}ON_3$. Calculated %: N 17.0

Hydrogenation of cis-3,4,4a,5,8,8a-Hexahydro-6,8a-dimethyl-1(2H)-naphthalenone (II). The ketone (II) (4 g), dissolved in 200 ml of absolute ether, was hydrogenated in presence of 0.3 g of a palladium catalyst (5% Pd supported on calcium carbonate). In the course of six hours, 571 ml of hydrogen (21°, 738 mm) was absorbed, corresponding to the hydrogenation of one double bond. The catalyst was filtered off, the solvent was distilled off, and the residue was vacuum-distilled. The product was 3.4 g of a substance having b.p. 83-85° (2.5 mm) and n_D^{20} 1.4860. Redistillation yielded 3 g of cis-octahydro-6,8a-dimethyl-1(2H)-naphthalenone (VIII), b.p. 82-83° (1.5 mm); n_D^{20} 1.4855; d_4^{20} 0.9660; Found MR 53.42; Calculated MR 53.23.

Found %: C 80.10; 80.28; H 11.38; 11.06

$C_{12}H_{20}O$. Calculated %: C 80.0 H 11.11

The semicarbazone, prepared in the usual way, melted at 207-208° (from 50% methanol).

Found %: N 17.43; 17.90

$C_{13}H_{23}ON_3$. Calculated %: N 17.71

1,2,3,4,4a,5,8,8a-Octahydro-1,6,8a-trimethyl-1-naphthol (V). A solution of methylmagnesium iodide was prepared from 4.8 g of methyl iodide and 0.7 g of magnesium in 25 ml of absolute ether in a three-necked flask fitted with stirrer, thermometer, dropping funnel, and reflux condenser. The solution was stirred at a temperature not exceeding +10° while slow addition was made of a solution of 4 g of cis-3,4,4a,5,8,8a-hexahydro-

6,8a-dimethyl-1(2H)-naphthalenone (II) in 10 ml of absolute ether. The mixture was then heated in a water bath at 40° for four hours. With cooling and stirring the reaction product was treated with 10 ml of 1 : 1 hydrochloric acid. The ether layer was separated, washed with a solution of sodium thiosulfate, and dried with magnesium sulfate. Ether was distilled off, and two successive vacuum fractionations of the residue yielded 3 g of pure 1,2,3,4,4a,5,8,8a-octahydro-1,6,8a-trimethyl-1-naphthol (V), b.p. 88-89° (1 mm); n_D^{20} 1.5051; d_4^{20} 0.9783; Found MR 59.23; Calculated MR 58.90.

Found %: C 80.28; 80.36; H 11.19; 11.12
$C_{13}H_{22}O$. Calculated %: C 80.41; H 11.30

Dehydration of 1,2,3,4,4a,8,8a-Octahydro-1,6,8a-trimethyl-1-naphthol (V). A mixture of 3 g of the octahydrotrimethylnaphthol (V) and 1.5 g of anhydrous potassium hydrogen sulfate was heated at 150-160° in a Claisen flask for one hour. A little water was added to dissolve the potassium hydrogen sulfate, and the dehydration product was extracted with ether. The extract was dried with magnesium sulfate, and ether was distilled off. Vacuum distillation of the residue yielded 1.5 g of the dehydration product, b.p. 86-90° (10 mm), which was redistilled over sodium and gave 1.2 g of 1,2,4a,5,8,8a-hexahydro-4,4a,7-trimethylnaphthalene (VI), b.p. 86-88° (10 mm); n_D^{20} 1.4580; d_4^{20} 0.9390. The hydrocarbon was dehydrogenated without further purification.

Dehydrogenation of 1,2,4a,5,8,8a-Hexahydro-4,4a,7-trimethylnaphthalene (VI). A mixture of 1.2 g of the hexahydrotrimethylnaphthalene (VI), 1 g of palladized charcoal (5% Pd), and 5 ml of cryoscopic benzene was heated for 36 hours at 350-360° in a metal ampoule. The catalyst was filtered off and washed with ether. Vacuum distillation of the residue remaining after removal of solvents yielded 0.6 g of 1,6-dimethylnaphthalene (VII), b.p. 105-107° (10 mm); n_D^{20} 1.5690. Its picrate, prepared in the usual way and crystallized from ethanol, had m.p. 113-114°, undepressed by admixture of known 1,6-dimethylnaphthalene picrate [8].

1-Ethynyl-1,2,3,4,4a,5,8,8a-Octahydro-6,8a-dimethyl-1-naphthol (IX). Liquid ammonia (600 ml) was introduced into a two-liter three-necked flask fitted with stirrer, thermometer, tube for passage of gas, and dropping funnel. Sodium (19 g) was added slowly at a temperature of −70°. The mixture was stirred for 30 minutes, and when the sodium had dissolved, dry acetylene was passed for two hours at 25-30 liters per hour. The resulting solution of sodium acetylide was stirred while, with continued passage of acetylene, a solution of 50 g of cis-3,4,4a,5,8,8a-hexahydro-6,8a-dimethyl-1(2H)-naphthalenone (II) in 100 ml of absolute ether was added slowly (over a period of 90 minutes). The mixture was then stirred for one hour, after which it was set aside overnight. The temperature of the reaction mixture was maintained at −70° throughout the reaction and during the night. On the next day much of the liquid ammonia was distilled off, and at −30° 250 ml of ether, 45 g of ammonium chloride (in small portions), and 270 ml of water were added. The ether layer was separated and the aqueous layer was extracted three times with 200-ml portions of ether. The united ether extract was washed twice with a 1% solution of hydrochloric acid and then dried with magnesium sulfate. The ether was distilled off, and the residue was vacuum-distilled. Two successive distillations yielded 49.5 g (87%) of the acetylenic alcohol (IX), b.p. 94-95° (1.5 mm); n_D^{20} 1.5210.

Found %: C 81.99; 81.91; H 9.89; 10.03
$C_{14}H_{20}O$. Calculated %: C 82.25; H 9.86

1-Ethyldecahydro-6,8a-dimethyl-1-naphthol (X). The acetylenic alcohol (IX) (2 g) was dissolved in 10 ml of ethanol and hydrogenated in presence of platinum oxide. In the course of three hours 660 ml of hydrogen (21°. 738 mm) was absorbed, which corresponds to the hydrogenation of three double bonds. Solvent was distilled off, and the hydrogenation product was distilled twice under reduced pressure. The product was 1.6 g of 1-ethyldecahydro-6,8a-dimethyl-1-naphthol (X), b.p. 103-104° (2 mm); n_D^{20} 1.5030.

Found %: C 79.78; 79.68; H 11.84; 11.98
$C_{14}H_{26}O$. Calculated %: C 79.98; H 12.20

1,2,3,4,4a,5,8,8a-Octahydro-6,8a-dimethyl-1-vinyl-1-naphthol (XI). 1-Ethynyl-1,2,3,4,4a,5,8,8a-octahydro-6,8a-dimethyl-1-naphthol (IX) (20 g) was dissolved in 250 ml of ethanol and hydrogenated over a palladium catalyst (5% Pd supported on calcium carbonate). In the course of two hours, 2.3 liters of hydrogen (21°, 736 mm) was absorbed, corresponding to the hydrogenation of one double bond, and the process was then discontinued. The catalyst was filtered off, solvent was distilled off, and the hydrogenation product was vacuum-distilled.

The following fractions were obtained:

Frac. I, b.p. 104-107° (3 mm); n_D^{20} 1.5160; 3.6 g
Frac. II, b.p. 107-108° (3 mm); n_D^{20} 1.5185; 15.2 g

Refractionation of Fraction II yielded 14.2 g (72%) of the pure ethylenic alcohol (XI), b.p. 107-107.5° (3 mm); n_D^{20} 1.5180.

Found %: C 81.25; 81.13; H 10.86; 10.62
$C_{14}H_{22}O_2$. Calculated %: C 81.42; H 10.62

1,2,4a,5,8,8a-Hexahydro-4a,7-dimethyl-4-vinylnaphthalene (XII). A mixture of 15 g of the ethylenic alcohol (XI) (b.p. 107-107.5°/3 mm, n_D^{20} 1.5180), 1.2 g of anhydrous potassium hydrogen sulfate, and 0.1 g of pyrogallol was heated at 130-135° and a residual pressure of 70 mm in a stream of nitrogen in a Claisen flask for 25 minutes. Water was distilled off, and the dehydration product was vacuum-distilled. The product was 12.4 g of the crude triene (XII), b.p. 111-114° (7 mm) and n_D^{20} 1.5155, and this was subjected to further dehydration by distillation over 0.5 g of anhydrous potassium hydrogen sulfate. The product, finally purified by distillation over sodium, was 9.1 g (about 70%) of pure 1,2,4a,5,8,8a-hexahydro-4a,7 dimethyl-4-vinylnaphthalene (XII), b.p. 109-110° (8 mm), n_D^{20} 1.5160.

Found %: C 88.85; 88.99; H 10.90; 10.86
$C_{14}H_{20}$. Calculated %: C 89.30; H 10.70

Condensation of 1,2,4a,5,8,8a-Hexahydro-4a,7-dimethyl-4-vinylnaphthalene (XII) with Maleic Anhydride. A mixture of 4 g of the triene (XII) (b.p. 109-110°/8 mm and n_D^{20} 1.5160) and 1.6 g of freshly distilled maleic anhydride was heated in presence of a little pyrogallol at 100° for three hours in a sealed glass tube. Unchanged triene and maleic anhydride were removed under reduced pressure, and the thick yellow oil that remained was distilled in a high vacuum. The following fractions were obtained:

Frac. I, b.p. 125-185° (0.025 mm); 1.2 g
Frac. II, b.p. 195-200° (0.025 mm); 3.6 g

Redistillation of Fraction II yielded 3 g of a thick light-yellow liquid, b.p. 197-200° (0.025 mm), corresponding in composition to the adduct (XIII).

Found %: C 75.95; 76.0 H 7.92; 8.09
$C_{18}H_{21}O_3$. Calculated %: C 75.76; H 7.80

The adduct (XIII) did not crystallize when treated with solvents and did not give a crystalline substance when hydrolyzed.

Condensation of 1,2,4a,5,8,8a-Hexahydro-4a,7-dimethyl-4-vinylnaphthalene (XII) with Dimethyl Fumarate. A solution containing 7 g of the triene (XII) and 5.3 g of dimethyl fumarate in 25 ml of benzene was heated in a metal ampoule at 200-210° for four hours. Solvent was distilled off, and crystals of dimethyl fumarate that separated were filtered off. The filtrate – a thick oil – was vacuum-distilled and yielded 4.1 g of the condensation product, b.p. 148-150° (0.02 mm), corresponding in composition to the adduct (XIV).

Found %: C 72.31; 72.38 H 8.45; 8.55
$C_{20}H_{28}O_4$. Calculated %: C 72.27; H 8.47

After hydrolysis of the product with 20% caustic potash solution no individual crystalline substances could be isolated.

SUMMARY

1. The condensation of isoprene with 2-methyl-2-cyclohexen-1-one (I) was studied, and it was shown that the main product of this reaction is the para isomer, cis-3,4,4a,5,8,8a-hexahydro-6,8a-dimethyl-1(2H)-naphthalenone (II), the structure of which was proved by its conversion into 1,6-dimethylnaphthalene (VII).

2. Condensation of the hexahydro-1(2H)-naphthalenone (II) with sodium acetylide in liquid ammonia gave a 90% yield of the acetylenic alcohol (IX), which was converted by selective hydrogenation into the ethylenic alcohol (XI). Dehydration of (XI) gave 1,2,4a,5,8,8a-hexahydro-4a,7-dimethyl-4-vinylnaphthalene (XII) in an overall yield, taken over all stages, of more than 50%.

3. The cis triene (XII) was condensed with maleic anhydride and with dimethyl fumarate, and mixtures of stereoisomeric adducts, (XIII) and (XIV), were obtained in high yield.

LITERATURE CITED

[1] I. N. Nazarov, G. P. Verkholetova, I. V. Torgov, and I. I. Zaretskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, No. 5, 920, 929;* I. N. Nazarov, L. I. Shmonina, and I. V. Torgov, Bull. Acad. Sci. USSR, Div. Chem Sci 1953, No. 6, 1074.**

[2] I. N. Nazarov, V. F. Kucherov, and V. M. Andreev, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 1, 78, 89.***

[3] I. N. Nazarov, L. D. Bergelson, I. V. Torgov, and S. N. Ananchenko, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, No. 5, 889. ****

[4] K. Alder, W. Vogt. Ann. 564, 109 (1949); L. Miller, D. Mann, J. Am. Chem. Soc. 72, 1484 (1950); J. Meek, R. Merrow, S. Cristol, J. Am. Chem. Soc. 74, 2667 (1952); I. N. Nazarov et al., J. Gen. Chem. 25, 88 (1955). *****

[5] J. Meek, R. Merrow, D. Ramay, J. Am. Chem. Soc. 73, 5563 (1952).

[6] I. N. Nazarov, I. V. Torgov, I. I. Zaretskaya, G. P. Verkholetova, et al., Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, No. 1, 78.******

[7] Organic Syntheses, Vol. 3, Foreign Lit. Press, Moscow, 1952, p. 187.

[8] I. Heilbron and H. M. Bunbury, Dictionary of Organic Compounds, Vol. 3, Foreign Lit. Press, Moscow, 1949, p. 492.

Received July 22, 1954

N. D. Zelinsky Institute of Organic
Chemistry of the USSR
Academy of Sciences

---

* Consultant's Bureau Translation, p.817, 827.

** Consultant's Bureau Translation, p. 955.

*** Consultant's Bureau Translation, p.67, 77.

**** Consultant's Bureau Translation, p.787.

***** Consultant's Bureau Translation, p.75.

****** Consultant's Bureau Translation, p.69.

STEREOCHEMISTRY OF CYCLIC COMPOUNDS

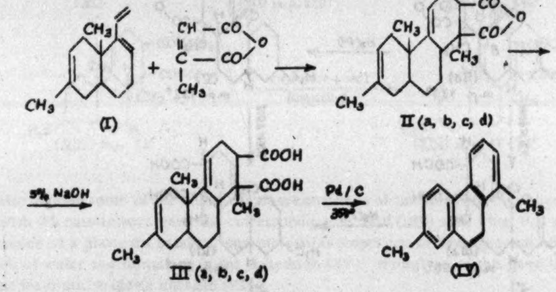
COMMUNICATION 8. CONDENSATION OF cis-1,2,4a,5,8,8a-HEXAHYDRO-4a,7-DIMETHYL-4-VINYLNAPHTHALENE WITH CITRACONIC ANHYDRIDE

I. N. Nazarov, V. F. Kucherov, and G. P. Kugatova

The diene condensations of 1-vinylcyclohexene with citraconic anhydride [1] and with dimethyl mesaconate [2] have made it possible to study some of the stereochemical transformations of bicyclic ortho-dicarboxylic acids and to make some interesting inferences relating to the dependence of their reactivities on their spatial structures. With the object of making a further study of the sterochemistry of cyclic compounds we have investigated the condensation of cis-1,2,4a,5,8,8a-hexahydro-4a,7-dimethyl-4-vinylnaphthalene (I) [3] with citraconic anhydride. When a mixture of these components (70-80% excess of diene) was heated at 100° for ten hours, a 30% yield was obtained of a mixture of four stereoisomeric crystalline anhydrides [(II); a, b, c, and d] which were separated by fractional crystallization.

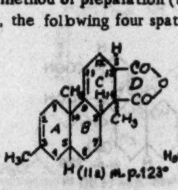
These isomeric anhydrides were isolated in the proportions 16 : 16 : 2 : 1, and when they were hydrolyzed with 5% caustic soda solution, the corresponding individual crystalline stereoisomeric cis acids [(III); a, b, c, and d] were obtained.

The proportions in which the crystalline isomers are formed in the diene synthesis were found to vary somewhat with temperature, and at 20° (10 days) very little of the isomer (IIc) was obtained. When reaction was at room temperature for one day and then at 100° for 10 hours, the amounts of the isomers (IIc) and (IId) were increased appreciably, though the isomers (IIa) and (IIb) were always the main reaction products.

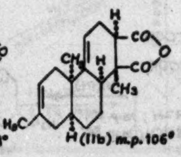


The identity of the ring structure present in the isomeric dicarboxylic acids [(III); a, b, c, and d] was proved by dehydrogenation over palladized charcoal (5% Pd) at 340-350°. The only product from all four isomers was 1,7-dimethylphenanthrene (IV), which was characterized as its picrate and styphnate. These results show that all four of the isomeric anhydrides (II) isolated in the synthesis described have the same phenanthrene skeleton and differ only in steric structure. These anhydrides were formed as a result of ortho addition; attempts to detect adducts formed by para addition in the products of the diene synthesis were not successful.

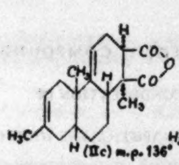
In accordance with the method of preparation (two-fold diene synthesis), for the anhydrides (II), which have five centers of asymmetry, the following four spatial configurations of the cis-cis series are possible:



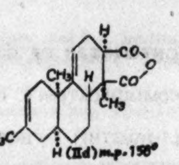
(IIa) m.p. 123°



(IIb) m.p. 106°



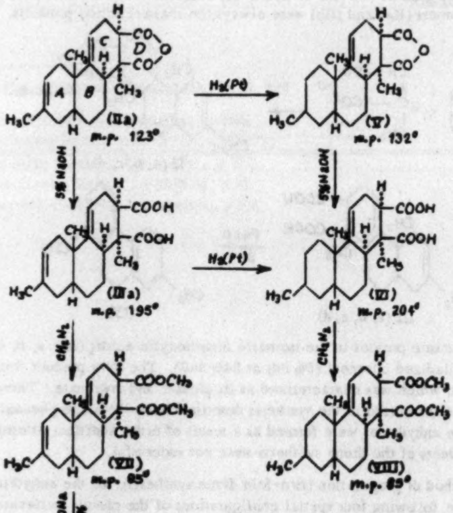
(IIc) m.p. 136°



(IId) m.p. 150°

In view of the relative mildness of the condensation conditions (up to 100°), it may be considered that each of the four isomeric anhydrides isolated has a double bond in the normal position (C-9)–(C-11)[*] and that the two isomers formed in predominating amounts, (IIa) and (IIb), have spatial structures corresponding, according to molecular models, to endo addition. These suppositions were fully confirmed by a study of the chemical transformations of the isomers, so that their spatial configurations have been proved.

When the cis anhydride (IIa) was hydrogenated in benzene or acetic anhydride in presence of a platinum catalyst, only one molecular porportion of hydrogen was absorbed, with formation of the individual anhydride (V), which gave the corresponding acid (VI) when hydrolyzed. The same acid was formed when the cis acid (IIIa), obtained by hydrolysis of the anhydride (IIa), was hydrogenated. Treatment of the cis acid (IIIa) with an ether solution of diazomethane gave the corresponding diester (VII), m.p. 95°, and this again absorbed only one molecular proportion of hydrogen when hydrogenated in presence of a platinum catalyst, the individual diester (VIII), m.p. 85°, being formed. In accordance with its cis structure, the diester (VII) gave a good yield of the trans acid (IX) when isomerized with sodium methoxide, and this acid gave the trans diester (X) with diazomethane and the individual trans acid (XI), formed by absorption of one molecular proportion of hydrogen, when hydrogenated over a platinum catalyst.



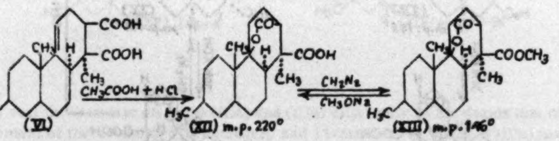
---

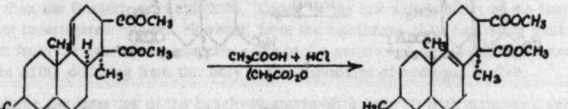
[*] Steroid numbering.

A characteristic feature of the compounds (IIa), (IIIa), (VII), and (IX) is the selectivity of hydrogenation., which only affects one double bond with formation of an individual product from each of these compounds. As shown previously [4], in such polycyclic compounds the double bond at (C-9) — (C-11) is considerably more difficult to hydrogenate than a double bond in the ring A. On this basis it may be supposed that in our experiments only the double bond in the ring A undergoes hydrogenation, and, owing to the cis configuration of the rings A and B, addition of hydrogen occurs from the unscreened side (opposite to the substituents at C-5 and C-10) and results in the cis configuration of the methyl group at C-3. As will be shown below, similar sterically selective hydrogenation of the double bond of the ring A is observed in all other similar compounds descibed in this communication. The position of the remaining double bond in the hydrogenation products was proved by subsequent lactonization and isomerization.

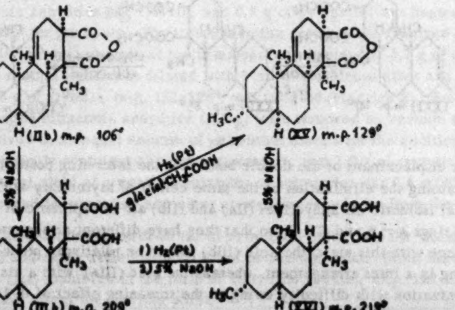
When the cis acid (VI) was heated with a mixture of acetic acid and dry hydrogen chloride, the cis lactone acid (XII), m.p. 220°, was formed. Titration of this showed that it contained one free carboxyl group, and treatment with diazomethane yielded the cis lactone ester (XIII). According to results obtained previously for bicyclic dicarboxylic acid [5], such lactonization is possible only when there is a double bond in the ring C. The lactone acid (XII) is a δ-lactone, for its ester (XIII) does not isomerize when boiled for a long time with sodium methoxide, but is hydrolyzed with formation of the original cis lactone acid (XII) in good yield.

The presence of a double bond at (C-9) — (C-11) in the acid (VI) was proved by the fact that the corresponding cis diester (VIII), treated under the conditions for double-bond migration (action of a mixture of glacial acetic acid, acetic anhydride, and hydrogen chloride), gave the new cis diester (XIV), m.p. 97-98°, having an interring double bond and identical with the substance obtained from the isomeric cis diester (XXV) (see below):

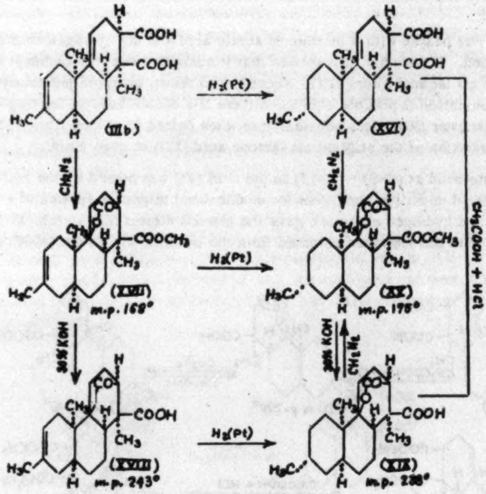

COOH
COOH
CH3 H
CH3
CH3COOH + HCl
H3C
(VI)
CO
O
COOH
(XII) m.p. 220°
CH2N2
CH3ONa
COOCH3
(XIII) m.p. 146°


COOCH3
COOCH3
CH3 H
CH3
H3C
(VIII) m.p. 85°
CH3COOH + HCl
(CH3CO)2O
COOCH3
COOCH3
CH3
(XIV) m.p. 97–98°

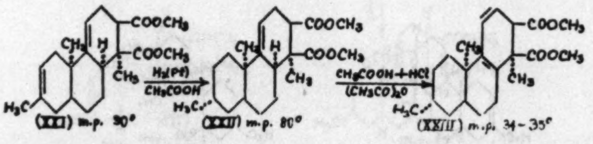
We have also studied some of the chemical transformations of the isomeric cis anhydride (IIb). Hydrolysis of this anhydride with 5% caustic soda gave the correspondigg cis acid (IIIb) and, when this was hydrogenated in acetic acid in presence of a platinum catalyst, one molecular proportion of hydrogen was absorbed with simultaneous elimination of water and formation of the anhydride (XV). Hydrolysis of this gave the pure cis acid (XVI), which was different from the isomeric cis acid (VI):


H
CO
O
CO
CH3 H
CH3
H3C
H (IIb) m.p. 106°
5% NaOH
H2(Pt)
glacial-CH3COOH
H (XV) m.p. 129°
5% NaOH
COOH
COOH
H (IIIb) m.p. 209°
1) H2(Pt)
2) 5% NaOH
H (XVI) m.p. 215°

Unlike the cis acids (IIIa) and (VI), the isomeric acids (IIIb) and (XVI) have a very strong tendency to undergo lactonization. Thus, when the cis acid (IIIb) was treated with a pure ethereal solution of diazomethane, the main product was not the diester, as it was for the isomeric cis acid (IIIa), but the crystalline cis lactone ester (XVIII), which undergoes hydrogenation with absorption of one molecular proportion of hydrogen and formation of the saturated lactone acid (XVI). Again, the main product of the reaction of diazomethane with the acid (XVI) is not the corresponding diester, but the saturated cis lactone ester (XX), which is obtained also when the cis lactone ester (XVII) is hydrogenated. Hydrolysis of the cis lactone ester (XX) gave the saturated cis lactone acid (XIX) in high yield.



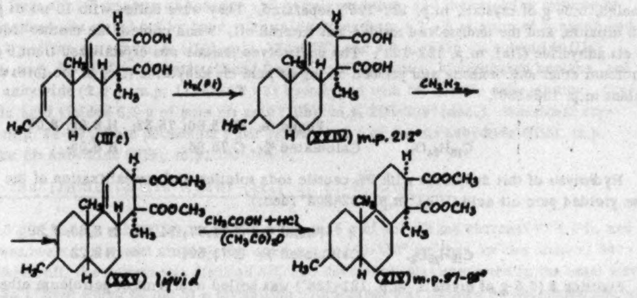
In the reaction of diazomethane with the cis acid (IIIb), only a small amount of the corresponding cis diester (XXI) was isolated. Hydrogenation of this diester in presence of a platinum catalyst yielded the cis diester (XXII) by absorption of one molecular proportion of hydrogen. Under the conditions for double-bond migration (action of a mixture of acetic anhydride, glacial acetic acid, and hydrogen chloride) the cis diester (XXII) gave the new diester (XXIII), m.p. 34-35°, having an inter-ring double bond and differing from the cis diester (XIV) obtained by the same method from the isomeric diester (VIII).



The fact that displacement of the double bond into the inter-ring position in the isomeric diesters (VIII) and (XXII), though causing the elimination of the same center of asymmetry at C-8, yields different products shows that the original isomeric cis anhydrides (IIa) and (IIb) are not epimeric at C-8, but differ in the relative configurations of the rings A – B and C – D, so that they have different arrangements of the angular methyl group at C-10. In accordance with this view, the acid (IIIb) should be relatively prone to lactonization, the 10-methyl and 13-carboxyl being in a trans arrangement, whereas the acid (IIIa), with a cis arrangement of these groups, should undergo lactonization with difficulty owing to the screening effect of the 10-methyl. Subsequent study of some reactions of the third isomeric cis acid (IIIc) enabled us to prove conclusively the spatial structures of the cis acids (IIIa) and (IIIc), as epimeric at C-8.

When the cis acid (IIIc) was hydrogenated over a platinum catalyst, again only one molecular proportion of hydrogen was absorbed with formation of the individual cis acid (XXIV), which readily gave the corresponding cis diester (XXV), a liquid, with diazomethane.

The formation of this cis diester was not accompanied by lactonization, and under the conditions of double-bond migration the diester readily gave the above-described cis diester (XIV), m.p. 97-98°, formed also by displacement of the double bond in the isomeric cis diester (VIII).



These facts show that the isomeric cis acids (IIIa) and (IIIc) differ only in the disposition of hydrogen at C-8, and the cis arrangement of the 10-methyl, 8-hydrogen, and 13-carboxyl in the acid (IIIc), makes it more stable to lactonization than the isomeric cis acid (IIIb). Owing to the low accessibility of the fourth isomeric cis acid (IIId), it was not investigated further. However, from the conditions of its formation there is no reason to suppose that it differs from the other three isomeric acids in the position of the double bond, and it should be an epimer of the acid (IIIb), differing from this only in the disposition of hydrogen at C-8.

The described diene condensation of the hexahydrovinylnaphthalene (I) with citraconic anhydride has a similar course, structurally and sterically, to the condensations of bicyclic dienes with α,β-unsaturated ketones previously investigated in our laboratory [4].

EXPERIMENTAL

Condensation of 1,2,4a,5,8,8a-Hexahydro-4a,7-dimethyl-4-vinylnaphthalene (I) with Citraconic Anhydride

1. A mixture of 15.2 g of 1,2,4a,5,8,8a-hexahydro-4a,7-dimethyl-4-vinylnaphthalene (b.p. 109-110.5°/8mm; n_D^{20} 1.5160) [3], 5.3 g of citraconic anhydride (n_D^{20} 1.4710), and 0.2 g of pyrogallol was heated in a nitrogen atmosphere in a sealed glass tube at 100° for ten hours. The liquid reaction product was dissolved in an equal volume of petroleum ether and the solution was set aside at room temperature overnight; 2.7 g of crystals, m.p. 108-121° separated (Fraction A). The mother liquor was diluted with 5 ml of petroleum ether and cooled to − 10°, and after 5-6 hours a further 0.5 g of crystals, m.p. 121-128°, was isolated (Fraction B). From the filtrate excess of the original diene and unchanged citraconic anhydride (3.5 g) were removed by vacuum distillation, and the thick yellow residue was dissolved in an equal volume of petroleum ether with the addition of 1 ml of absolute benzene. The solution was set aside overnight at room temperature, and 3.2 g of crystals melting at 95-107° separated (Fraction C). The total yield of crystalline mixtures of anhydrides was 6.4 g (45% on the citraconic anhydride). We did not succeed in separating any other crystalline anhydrides from the liquid residue (5 g).

Fraction A (2.7 g) was boiled for 1-2 minutes with 50 ml of petroleum ether, and the undissolved portion was filtered off (1.4 g, m.p. 117-121°) and again boiled with 25 ml of petroleum ether. From the cooled filtrates 1.8 g of pure crystalline cis anhydride (IIa) separated in the form of short fine needles, m.p. 122-123°. Recrystallization from petroleum ether did not affect the melting point.

Found %: C 76.0 75.80; H 8.10; 8.30

$C_{19}H_{24}O_3$. Calculated %: C 75.96; H 8.05

Hydrolysis of the cis anhydride (IIa) was effected by boiling 0.22 g with 3 ml of 5% caustic soda solution. Acidification yielded 0.2 g of acid, m.p. 184-186°. Two successive crystallizations from 60% methanol yielded 0.17 g of pure cis acid (IIIa), m.p. 194-195° (dec).

Found %: C 71.70; 71.78; H 8.30; 8.25

$C_{19}H_{26}O_4$. Calculated %: C 71.56; H 8.23

The crystalline substance (0.7 g) that remained, undissolved by petroleum ether, after the separation of the cis anhydride (IIa) was dissolved by prolonged boiling in 25 ml of petroleum ether. When the solution was cooled, 0.36 g of crystals, m.p. 120-125°, separated. They were boiled with 10 ml of petroleum ether for 1-2 minutes, and the undissolved residue was filtered off. When cooled, the mother liquor yielded 0.2 g of the cis anhydride (IIa), m.p. 122-123°. The undissolved residue was crystallized from 6 ml of a 5 : 1 mixture of petroleum ether and benzene and yielded 50 mg of pure cis anhydride (IIc) in the form of small plates having a constant m.p. 135-136°.

Found %: C 75.60; 75.82; H 8.09; 8.09

$C_{19}H_{24}O_3$. Calculated %: C 75.96; H 8.05

Hydrolysis of this anhydride with 5% caustic soda solution and crystallization of the product from aqueous acetone yielded pure cis acid (IIIc), m.p. 202-203° (dec.).

Found %: C 71.67; 71.48; H 8.35; 8.39

$C_{19}H_{26}O_4$. Calculated %: C 71.56; H 8.23

Fraction B (0.5 g of crystals, m.p. 121-128°) was boiled with 5 ml of petroleum ether for 3-5 minutes, and the undissolved portion was filtered off. The cooled filtrate yielded a further 0.1 g of the cis anhydride (IIa), m.p. 122-123°. The substance not dissolved by petroleum ether (0.17 g, m.p. 123-129°) was crystallized twice from a 5 : 1 mixture of petroleum ether and benzene and yielded 10 mg of pure crystalline cis anhydride (IId) in the form of long needles having a constant m.p. of 156-157°.

Found %: C 76.16; H 8.02

$C_{19}H_{24}O_3$. Calculated %: C 75.96; H 8.05

Hydrolysis of this anhydride with 5% caustic soda solution, followed by crystallization of the product from aqueous acetone, yielded pure cis acid (IIId), m.p. 180-181° (dec.).

Found %: C 71.26; H 8.33

$C_{19}H_{26}O_4$. Calculated %: C 71.56; H 8.23

Fraction C (3.2 g of crystals, m.p. 95-107°) was recrystallized from ether and yielded 2.2 g of an apparently pure anhydride (large plates, m.p. 120-130°). Further crystallizations from various solvents did not narrow the melting range. This anhydride was hydrolyzed at the boil with excess of 5% caustic soda solution, and the crystalline acid was recrystallized from 5% acetic acid. The product was 1.6 g of pure cis acid (IIIb), melting constantly at 208-209°.

Found %: C 71.81; 71.87; H 8.45; 8.40

$C_{19}H_{26}O_4$. Calculated %: C 71.56; H 8.23

The cis acid (IIIb) was readily converted into its anhydride by treatment with acetic anhydride at the boil for two hours. Acetic anhydride was distilled off, and the crystalline residue was crystallized twice from petroleum ether. The product was pure cis anhydride (IIb), melting constantly at 105-106.5°.

Found %: C 75.80; 76.0; H 8.23; 8.18

$C_{19}H_{24}O_3$. Calculated %: C 75.96; H 8.05

The liquid residue (5 g) remaining after separation of the crystalline anhydride fractions (A, B, and C) was hydrolyzed and yielded 2.5 g of acid. Crystallization of this from 60% methanol yielded 1.4 g of pure cis acid (IIIa), m.p. 194-195° (dec.).

2. A mixture of 20 g of 1,2,4a,5,8,8a-hexahydro-4a,7-dimethyl-4-vinylnaphthalene (I), 7 g of citraconic anhydride, and 0.2 g of pyrogallol was sealed in a tube in a nitrogen atmosphere. The mixture was set aside at room temperature, and after some time, during which it was periodically shaken, it became homogeneous. After 15-18 hours the reaction mixture was heated to 100° and kept at this temperature for ten hours. The solution was diluted with an equal volume of petroleum ether and set aside overnight; 2.1 g of crystals, m.p. 110-119°

separated (Fraction A). The filtrate, after being diluted with 5 ml of petroleum ether and cooled to −20°, yielded a further 0.4 g of crystalline adduct, m.p. 114-124° (Fraction B).

Excess of the triene (I) and unchanged citraconic anhydride were distilled from the filtrate under reduced pressure, and the liquid residue was dissolved in an equal volume of petroleum ether with the addition of 2-3 ml of benzene. The crystals that separated after two hours at room temperature were filtered off, and 4.1 g of adduct melting at 85-103° was obtained (Fraction C). Petroleum ether was partially removed from the mother liquor, and this then yielded a further 3.1 g of crystals, m.p. 84-89° (Fraction D).

Fractional crystallization of Fraction A from petroleum ether, as described above, yielded 1.4 g of cis anhydride (IIa), m.p. 122.5-123.5°, and 0.15 g of cis anhydride (IIc), m.p. 135-136°. Fraction B (0.4 g of crystals) was recrystallized from a 1 : 5 mixture of benzene and petroleum ether, and the resulting mixture of crystals (large plates and needles) was sorted out by hand. Crystallizations from a 1 : 5 mixture of benzene and petroleum ether yielded 0.1 g of the cis anhydride (IIc), m.p. 135-136°, and 0.2 g of the cis anhydride (IId), m.p. 156-157°. Fraction C, m.p. 85-103°, was recrystallized from a 1 : 1 mixture of benzene and heptane, and the resulting nonhomogeneous anhydride (2.6 g, m.p. 113-120°) was hydrolyzed with 5% caustic soda solution. Crystallization from 50% acetic acid yielded 2.2 g of pure cis acid (IIIb), m.p. 208-209° (dec.). Fractional crystallization of Fraction D, m.p. 84-89°, from petroleum ether yielded 1.1 g of the cis anhydride (IIIa), m.p. 122-123°, and 0.15 g of pure cis anhydride (IIIb), m.p. 105-106.5°.

Dehydrogenation of the Isomeric cis Acids (III; a, b, c, and d)

1. A mixture of 0.3 g of the cis acid (IIIa), m.p. 194-195°, 0.15 g of palladized charcoal (5 % Pd), and 7 ml of absolute benzene was heated in a steel ampoule for one hour at 140-150° and then for two hours at 340-350°. The catalyst was filtered off, the solvent was distilled off, and the residue was converted in the usual way into a picrate (m.p. 122-125°), from which 80 mg of a crystalline hydrocarbon was isolated by decomposition with alkali. Crystallization from a little absolute methanol yielded 65 mg of 1,7-dimethylphenanthrene, m.p. 83-84°, which gave a picrate, m.p. 130-131°, and styphnate, m.p. 158-159°.

2. In a similar way, dehydrogenation of 0.3 g of the cis acid (IIIb) yielded, after crystallization from methanol, 75 mg of 1,7-dimethylphenanthrene, m.p. 83-84°, which gave a styphnate melting at 157-158°. The isomeric cis acids (IIIc) and (IIId) were dehydrogenated in the same way. The constants of the hydrocarbons obtained, and of their derivatives, are given in the following table.

TABLE

Hydrocarbon	M.p. (°C)		
	of hydrocarbon	of picrate	of styphnate
1,7-Dimethylphenanthrene [6]	85	131-132	159
Hydrocarbon from (IIIa)	83-84	130-131	158-159
Hydrocarbon from (IIIb)	83-84	–	157-158
Hydrocarbon from (IIIc)	–	130-131	–
Hydrocarbon from (IIId)	80-82	129-130	–
2,6-Dimethylphenanthrene [6]	101	154	–

Hydrogenation of the cis Anhydride (IIa)

The cis anhydride (IIa) (0.5 g; m.p. 122.5-123.5°) was dissolved in 50 ml of cryoscopic benzene and hydrogenated in presence of a platinum catalyst. In the course of one hour 85 ml of hydrogen (24°, 744 mm) was absorbed (one molecular proportion), and hydrogenation then ceased. Catalyst was separated and solvent was distilled off, and crystallization of the crystalline residue from petroleum ether yielded 0.37 g of pure cis anhydride (V), m.p. 131-132°.

Found %: C 75.51; 75.26; H 8.68; 8.63

$C_{19}H_{26}O_3$. Calculated %: C 75.45; H 8.67

a) The cis acid (IIIa) (0.2 g; m.p. 194-195°) was dissolved in 20 ml of glacial acetic acid and hydrogenated over a platinum catalyst. Hydrogenation ceased when 20 ml (one molecular proportion) of hydrogen had been absorbed. The solvent was distilled off, and the liquid residue was hydrolyzed with 5% caustic soda solution. The product was 0.16 g of the cis acid (VI), which after crystallization from 70% aqueous acetone melted constantly (with decomposition) at 203-204°.

Found %: C 71.05; 71.29; H 8.84; 8.87

$C_{19}H_{28}O_4$. Calculated %: C 71.22; H 8.80

b) A mixture of 0.15 g of the cis anhydride (V) and 12 ml of 5% caustic soda solution was refluxed until a solution was obtained. Acidification of the solution yielded 0.1 g of the cis acid (VI), m.p. 202-203°, undepressed in an admixture of the product of the previous experiment.

cis Diester (VII)

A suspension of 0.3 g of the cis acid (IIIa) in 10 ml of ether was treated with excess of an ether solution of diazomethane. The liquid residue remaining after removal of ether crystallized when treated with petroleum ether, and 0.25 g of the cis diester (VII), melting constantly at 95-95.5°, was obtained.

Found %: C 72.91; 72.75; H 8.75; 8.85
$C_{21}H_{30}O_4$. Calculated %: C 72.79; H 8.72

cis Diester (VIII)

a) The cis diester (VII) (0.1 g; m.p. 95-95.5°) was dissolved in 7 ml of glacial acetic acid and hydrogenated over a platinum catalyst. Hydrogenation ceased when 8.5 ml (one molecular proportion) of hydrogen had been absorbed. The solvent was distilled off, and the liquid residue gradually solidified when evaporated under reduced pressure with ligroin. The completely solid material was crystallized from petroleum ether, and 0.07 g of pure cis diester (VIII), m.p. 85.5-86°, was obtained.

Found %: C 71.99; 72.27; H 9.35; 9.21
$C_{21}H_{32}O_4$. Calculated %: C 72.37; H 9.25

b) When an ether suspension of 0.1 g of the cis acid (VI) was treated with an ether solution of diazomethane, the product, obtained after removal of ether and crystallization of the residue from petroleum ether, was 0.08 g of the diester (VIII), m.p. 85-86°, identical with the product of the previous experiment.

Isomerization of the cis Diester (VII)

The cis diester (VII) (0.4 g) was added to a solution of 1 g of sodium in 25 ml of absolute methanol, and the solution was boiled for 18 hours. The bulk was reduced by one-quarter by removal of methanol, 8 ml of water was added, and the solution was again boiled for five hours, after which it was evaporated down in a porcelain dish on a water bath to a thick slurry. The precipitate of salts was filtered off and suspended in water. Acidification of the suspension to Congo red yielded 0.35 g of acid, m.p. 196-199°, which was crystallized twice from 60% aqueous methanol and yielded 0.2 g of pure trans acid (IX), m.p. 222-224° (dec.).

Found %: C 71.70; 71.67; H 8.09; 8.07
$C_{19}H_{26}O_4$. Calculated %: C 71.56; H 8.23

The trans acid (IX) was treated with an ether solution of diazomethane and the product was crystallized from petroleum ether. A good yield of the trans diester (X), m.p. 79.5-80°, was obtained.

Found %: C 72.64; 72.84; H 8.80; 8.72
$C_{21}H_{30}O_4$. Calculated %: C 72.79; H 8.72

Hydrogenation of the trans Acid (IX)

The trans acid (IX) (0.2 g; m.p. 222-224°) was dissolved in 12 ml of glacial acetic acid and hydrogenated over a platinum catalyst. Only one molecular proportion of hydrogen was absorbed (17 ml). Solvent was distilled off, and the crystalline residue was washed on the filter with a 1 : 1 mixture of benzene and petroleum ether. Recrystallization from 80% aqueous acetone yielded 0.16 g of the trans acid (XI), m.p. 228-229.5° (dec.), depressed by admixture of the original acid (200-210°).

Found %: C 71.20; 71.38; H 8.89; 8.97
$C_{19}H_{28}O_4$. Calculated %: C 71.22; H 8.80

cis Lactone Acid (XII)

A mixture of 0.2 g of the cis acid (VI), m.p. 203-204° and 2 ml of glacial acetic acid saturated with dry hydrogen chloride was heated at 60° for one hour. The crystals remaining after removal of acetic acid by distillation were washed on the filter with benzene. Crystallization from 70% aqueous methanol yielded 0.15 g of pure cis lactone acid (XII), m.p. 219-220°.

Found %: C 71.03; 71.28; H 8.94; 9.03
$C_{19}H_{28}O_4$. Calculated %: C 71.22; H 8.80

Found: M 329.1
Calculated: M 320.4 (by titration with NaOH)

with diazomethane. Hydrolysis of the cis lactone ester (XX) at the boil with excess of 30% caustic potash solution gave a good yield of the original cis lactone acid (XIX), m.p. 237-238°.

Action of Diazomethane on the cis Acid (IIIb)

A pure dry ethereal solution of diazomethane was added in slight excess, with cooling and stirring, to a suspension of 0.5 g of the cis acid (IIIb) in 25 ml of ether. After one hour at room temperature, ether was distilled off and the crystalline residue was boiled with 10 ml of petroleum ether; undissolved material was filtered off. The filtrate, when cooled, yielded 0.1 g of crystals, which were recrystallized from petroleum ether and then melted constantly at 89-90° and corresponded in composition to the cis diester (XXI).

Found %: C 73.02; 72.79; H 8.85; 8.85
$C_{21}H_{30}O_4$. Calculated %: C 72.79; H 8.72

The substance that was not dissolved by petroleum ether (0.4 g) was crystallized from a 2 : 1 mixture of ether and petroleum ether and yielded 0.35 g of pure cis lactone ester (XVII), m.p. 168-169°.

Found %: C 72.14; 72.40; H 8.22; 8.37
$C_{20}H_{28}O_4$. Calculated %: C 72.25; H 8.49

Hydrogenation of the cis Lactone Ester (XVII)

The cis lactone ester (XVII) (0.1 g; m.p. 168-169°) was dissolved in 5 ml of glacial acetic acid and hydrogenated over a platinum catalyst. Hydrogenation ceased when 9 ml (one molecular proportion) of hydrogen had been absorbed. The acetic acid was distilled off under reduced pressure, and the crystalline residue was recrystallized from 60% aqueous methanol. The product was 0.08 g of the cis lactone ester (XX), m.p. 175-176°, identical with that obtained previously by the action of diazomethane on the cis acid (XVI).

Hydrolysis of the cis Lactone Ester (XVII)

A mixture of 0.1 g of the cis lactone ester (XVII) and 3 ml of 30% caustic potash solution was boiled until solution was complete (six hours). Acidification precipitated a crystalline substance, and crystallization of this from 60% aqueous acetone yielded 0.07 g of pure cis lactone acid (XVIII), melting constantly at 243-244°.

Found %: C 71.56; 71.54; H 8.44; 8.46
$C_{19}H_{26}O_4$. Calculated %: C 71.56; H 8.23

Hydrogenation of 50 mg of this cis lactone acid in acetic acid in presence of a platinum catalyst and crystallization of the product from 60% aqueous acetone yielded 35 mg of the cis lactone acid (XIX), m.p. 238-239°, identical with the product obtained previously by the lactonization of the cis acid (XVI).

Hydrogenation of the cis Diester (XXI)

The cis diester (XXI) (80 mg; m.p. 90-91°) was dissolved in 3 ml of glacial acetic acid and hydrogenated over a platinum catalyst. One molecular proportion (6.5 ml) of hydrogen was absorbed. Crystals remaining after removal of acetic acid were recrystallized from petroleum ether, and yielded 60 mg of pure cis diester (XXII), melting constantly at 79-80°.

Found %: C 72.25; 72.37; H 9.24; 9.38
$C_{21}H_{32}O_4$. Calculated %: C 72.37; H 9.25

Displacement of the Double Bond in the cis Diester (XXI)

The cis diester (XXI) (0.1 g; m.p. 89-90°) was heated for one hour at 50° with 1 ml of a 1 : 1 mixture of acetic anhydride and glacial acetic acid saturated with dry hydrogen chloride. The liquid remaining after removal of solvents by distillation was dissolved in petroleum ether, and from this solution, when cooled with solid carbon dioxide, 60 mg of the isomeric cis diester (XXIII), m.p. 34-35°, separated.

Found %: C 72.48; H 9.01
$C_{21}H_{32}O_4$. Calculated %: C 72.37; H 9.25

Hydrogenation of the cis Acid (IIIc)

The cis acid (IIIc) (0.3 g; m.p. 203-204°) was dissolved in 10 ml of glacial acetic acid and hydrogenated over a platinum catalyst. Only one molecular proportion of hydrogen was absorbed (39 ml at 20° and 740 mm). Acetic acid was distilled off, and the semisolid residue was hydrolyzed at the boil with 5 ml of 5% caustic soda solution. The resulting acid was recrystallized from 60% aqueous methanol, and 0.27 g of the cis acid (XXIV), m.p. 210-212° (dec.), was obtained.

cis Lactone Ester (XIII)

An ether suspension of 0.1 g of the cis lactone acid (XII) was treated with an ether solution of diazomethane. Ether was distilled off, and the reaction product was crystallized from petroleum ether. The product was 0.07 g of pure cis lactone ester (XIII) having a constant melting point of 145-146°.

Found %: C 71.87; 71.85; H 9.06; 9.04

$C_{20}H_{30}O_4$. Calculated %: C 71.81; H 9.04

The cis lactone ester (XIII), after prolonged boiling with excess of 10% sodium methoxide followed by hydrolysis, gave the original cis lactone acid (XII), m.p. 218-220°, in good yield.

Displacement of the Double Bond in the cis Diester (VIII)

A solution of 0.2 g of the cis diester (VIII) in 1 ml of a 1 : 1 mixture of acetic anhydride and acetic acid saturated with dry hydrogen chloride was heated at 60° for one hour. A liquid remained after removal of acetic acid and acetic anhydride under reduced pressure and this crystallized when treated with petroleum ether. Crystallization from petroleum ether gave 0.15 g of pure isomeric cis diester (XIV), m.p. 97-98°.

Found %: C 72.40; 72.45; H 8.98; 9.13

$C_{21}H_{32}O_4$. Calculated %: C 72.37; H 9.25

Hydrogenation of the cis Acid (IIIb)

a) The cis acid (IIIb) (1.0 g; m.p. 208-209°) was dissolved in 70 ml of glacial acetic acid and hydrogenated over a platinum catalyst. The volume of hydrogen absorbed was 124 ml (20°, 740 mm), corresponding to the hydrogenation of one double bond; no further hydrogenation occurred under these conditions. The catalyst was filtered off, solvent was distilled off under reduced pressure, and the nonhomogeneous crystalline product was hydrolyzed at the boil with 10 ml of 5% caustic soda solution. Acidification yielded 0.9 g of substance, and crystallization of this from 40% aqueous acetone yielded 0.5 g of pure cis acid (XIV), m.p. 218-219° (dec.).

Found%: C 71.20; 71.35; H 8.92; 8.74

$C_{19}H_{28}O_4$. Calculated%: C 71.22; H 8.80

b) In a similar way; 0.3 g of the cis acid (IIIb) was hydrogenated in 10 ml of glacial acetic acid. After removal of solvent the crystalline product was washed on the filter with petroleum ether and recrystallized from a 1 : 2 mixture of benzene and petroleum ether. The product was 0.15 g of pure cis anhydride (XV), m.p. 129-130°.

Found %: C 75.26; 75.17; H 8.93; 8.86

$C_{19}H_{26}O_3$. Calculated %: C 75.45; H 8.67

When hydrolyzed, this cis anhydride gave a good yield of the cis acid (XIV), m.p. 217-219° (dec.).

cis Lactone Acid (XIX)

A solution of 0.2 g of the cis acid (XVI), m.p. 218-219°, in 2 ml of glacial acetic acid saturated with dry hydrogen chloride was heated at 60° for one hour. Acetic acid was distilled off under reduced pressure, and crystallization of the crystalline residue from 60% aqueous acetone yielded 0.15 g of the cis lactone acid (XIX), m.p. 238-239°.

Found %: C 71.15; 71.33; H 8.82; 8.70

$C_{19}H_{28}O_4$. Calculated %: C 71.22; H 8.80

Found: M 331

Calculated: M 320.4 (by titration with NaOH)

Action of Diazomethane on the cis Acid (XVI)

A suspension of 0.20 g of the cis acid (XVI) in ether was cooled and stirred while a slight excess of a dry purified ethereal solution of diazomethane was added. After one hour ether was removed under reduced pressure. Crystallization of the crystalline reaction product from a 3 : 1 mixture of diethyl ether and petroleum ether yielded 0.17 g of the cis lactone ester (XX), m.p. 175-176°.

Found %: C 71.63; 71.55; H 9.00; 9.05

$C_{20}H_{30}O_4$. Calculated %: C 71.81; H 9.04

The same cis lactone ester (XX) was obtained quantitatively when the cis lactone acid (XIX) was treated

Found %: C 71.29; 71.19; H 8.75; 8.86

$C_{19}H_{22}O_4$. Calculated %: C 71.22; H 8.80

The cis Diester (XXV), and its Isomerization into the cis Diester (XIV)

A suspension of 0.2 g of the cis acid (XXIV) in ether was treated with excess of an ether solution of diazomethane. After removal of ether the liquid cis diester (XXV) remained, and this did not solidify when treated with various solvents and when cooled. It was dissolved in 2 ml of a 1 : 1 mixture of acetic acid and acetic anhydride saturated with dry hydrogen chloride, and the solution was heated at 60° for one hour. Solvents were removed under reduced pressure, and the liquid product solidified when evaporated under reduced pressure with petroleum ether. Crystallization from petroleum ether yielded 0.1 g of an individual crystalline substance, m.p. 97-98°, and this was found to be identical with the cis diester (XIV), which was obtained previously as a result of double-bond migration in the cis diester (VIII).

SUMMARY

1. The condensation of 1,2,4a,5,8,8a-hexahydro-4a,7-dimethyl-4-vinylnaphthalene (I) with citraconic anhydride was studied, and all four theoretically possible stereoisomeric cis anhydrides (II; a, b, c, and d) were isolated. The structures of these, as ortho-addition products, were proved by dehydrogenation of the corresponding cis acids (III; a, b, c, and d) into 1,7-dimethylphenanthrene. No diene-synthesis products formed by para addition were detected.

2. When the isomeric cis acids (IIIa, IIIb, and IIIc) and their derivatives (anhydrides, diesters, lactone acids, and lactone esters) were hydrogenated in presence of a platinum catalyst, only one molecular proportion of hydrogen was absorbed – by reaction at the double bond in the ring A. Under these conditions the second double bond (in the ring C) was not hydrogenated. A peculiar feature in all of these hydrogenation reactions was their steric selectivity, which resulted in the formation of individual hydrogenated derivatives in which the 3- and 10-methyl groups always have a cis arrangement.

3. Isomerization of the cis diester (VII) with sodium methoxide yielded the trans acid (IX), which was hydrogenated to the trans acid (XI).

4. The isomeric cis acids (IIIa) and (IIIb), which were obtained in predominating amount, differ in the disposition of the substituents at C-5 and C-10, for double-bond migration in the diesters (VIII) and (XXII) yields different cis diesters (XIV) and (XXIII) having an inter-ring double bond. On the other hand, displacement of the double bond in the cis diester (VIII) and (XXV) gives, in each case, the same cis diester (XIV), so that the isomeric cis acids (IIIa) and (IIIc) differ only in the disposition of hydrogen at C-8.

5. The cis acids (IIIb) and (XVI), unlike the isomeric cis acids (IIIa) and (VI), are extremely prone to lactonization, and even when treated with diazomethane they give mainly the cis lactone esters (XVII) and (XX), instead of the corresponding diesters. This difference is in accord with their spatial structures; in the cis acid (IIIb), in which there is a trans arrangement of the 10-methyl and 13-carboxyl, the 10-methyl has no screening effect, and as a result lactonization is facilitated.

LITERATURE CITED

[1] I. N. Nazarov, V. F. Kucherov, and V. M. Andreev, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 1, 78. (See Consultant's Bureau Translation, p 67).

[2] I. N. Nazarov, V. F. Kucherov, and V. M. Andreev, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 1. 89.

[3] I. N. Nazarov and G. P. Kugatova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No 3, 480. (See (Consultant's Bureau Translation, p 27).

[4] I. N. Nazarov, G. P. Verkholetova, I. V. Torgov, I. A. Zaretskaya, et al., Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, 930, No. 6, 1074. (See Consultant's Bureau Translation, p955).

[5] I. N. Nazarov, V. F. Kucherov, and V. M. Andreev, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 1955, No. 2, 289. (See Consultant's Bureau Translation, p257).

[6] R. Haworth, B. Letsky, C. Mavin, J. Chem. Soc. 1932, 1789; R. Haworth et al., J. Chem. Soc. 1934, 459.

Received July 22, 1954

N. D. Zelinsky Institute of Organic Chemistry of the USSR Academy of Sciences

BLANK
PAGE

HIGH-TEMPERATURE REACTIONS OF METHYLCYCLOHEXANE IN A CONTINUOUS-FLOW SYSTEM IN PRESENCE OF METALS OF THE PALLADIUM GROUP AND OF HYDROGEN AT HIGH PRESSURE *

N. I. Shuikin, Kh. M. Minachev, L. M. Feofanova, E. G. Treshchova,
T. P. Yudkina, and A. E. Agronomov

The reactions of hydrogenation, dehydrogenation, and aromatization of normal alkanes and the hydrogenolysis of cyclopentanes in presence of metals of Group VIII have been thoroughly studied [1-12]. These catalysts have a valuable selective action in many reactions, and wide use has been made of this peculiarity in the establishment of some of the general laws of heterogeneous catalysis. One theory of organic heterogeneous catalysis – the multiplet theory of Baladin – is largely based on experimental material obtained in the investigation of the specific properties of metal catalysts.

In recent years papers have appeared that relate to the application of platinum and nickel catalysts in the transformation of hydrocarbons at high temperature in presence of hydrogen at high pressure. Thus, in several papers [16-19] it is recommended that platinum should be applied on the industrial scale for the reforming of straight-run gasolines with the object of improving them as motor fuels, and the behavior, under these conditions, of some individual hydrocarbons is described.

Shuikin, Berdnikova, and Novikov [20, 21] investigated the catalytic reactions of several alicyclic hydrocarbons at 460° in presence of platinized alumina and hydrogen at 15-20 atm in a flow system. The results that they obtained are given in Table 1.

It will be seen from Table 1 that at high temperatures and in presence of hydrogen at high pressure the investigated cycloalkanes undergo various reactions with formation of a complex mixture of hydrocarbons. The mechanism proposed by the authors for these reactions was based on the methylene breakdown of some of the cycloalkane molecules and the methylation of the original hydrocarbon and its catalysis-reaction products by methylene radicals arising in this way. It must be pointed out that, already in 1934, Zelinsky and Shuikin [22] observed the formation of toluene, xylenes, and methyl- and dimethyl-cyclohexanes, with participation of methylene radicals, in the catalytic treatment of cyclohexane in presence of $Ni-Al_2O_3$ at 330-350°.

Ciapetta and Hunter [23] have investigated the reactions of normal alkanes, cyclopentanes, and cyclohexanes in presence of nickel, cobalt, iron, and platinum supported on various carriers at 250-480° in presence of hydrogen at high pressure in a flow system. The most active catalyst for the isomerization of normal alkanes was found to be 5% nickel on aluminosilicate.

Thus, the use of hydrogen at high pressure and temperatures of the order of 450° in the catalytic treatment of hydrocarbons of various classes in presence of metal-oxide catalysts results in the occurrence of reactions that occur either not at all or only to a slight extent when atmospheric pressure and temperatures not above 300-310° are used.

In the present paper we present new experimental material obtained in an investigation of the transformations of methylcyclohexane in contact with platinum, palladium, rhodium, and ruthenium catalysts. Alumina and silica gel were used as carriers. The properties of finely dispersed palladium at high temperatures and in presence of hydrogen at high pressure have received almost no study. The catalytic properties of rhodium and ruthenium in the reactions of hydrocarbons in general have been studied very little.

---

* The spectroscopic part of the work was carried out in the Molecular Spectroscopy Laboratory of the Chemistry Faculty of the Moscow State University under the supervision of V. M. Tatevsky, to whom the authors are grateful for help in assessing the results of the spectroscopic determinations.

TABLE 1

Compositions of Catalyzates Obtained as the Result of Reactions of Cyclopentane, Methylcyclopentane, and Cyclohexane in presence of Platinized Alumina Catalyst and of Hydrogen at High Pressure at 460°

Composition of catalysis products (% on original cycloalkane)	Original hydrocarbon		
	Cyclopentane	Methylcyclopentane	Cyclohexane
Degree of conversion	71.2	67.8	98.8
Gas and losses	22.6	8.3	6.6
Liquid catalyzate	77.4	91.7	93.4
Aromatic hydrocarbons	7.2	29.5	79.8
Cyclopentane	–	1.1	0.7
Methylcyclopentane	1.3	–	6.0
Pentane	34.5	3.1	2.6
2-Methylbutane	10.0	1.3	0.5
Other branched paraffins			
Those containing tertiary C	–	18.2	1.3
Those containing quaternary C	–	5.3	1.0
Unchanged cycloalkane	22.8	32.0	1.2
Not accounted for	1.6	1.2	0.3

EXPERIMENTAL

Carriers. Commercial silica gel was ground to particles of the size of 1.5-2.0 mm, treated several times with 1 : 1 hydrochloric acid, washed with distilled water until tests for chloride were negative, dried, and heated at 500° for three hours in a muffle. Alumina was first heated under the same conditions as the silica gel.

Catalysts. All catalysts were prepared under the same conditions. The carrier was impregnated with a dilute solution of H_2PtCl_6, $PdCl_2$, H_3RhCl_6, or $(NH_4)_2RuCl_5NO$ at room temperature, and then dried at 110° for 4-5 hours. It was then placed in the steel tube of an electric furnace and reduced with electrolytic hydrogen with gradual rise in temperature to 225-340°. The activity of the catalyst was determined by the extent of dehydrogenation of cyclohexane at 300-305°; with the exception of the ruthenium catalyst, all were extremely active.

Determination of the Specific Surfaces of Catalysts and Carriers. The specific surfaces of the catalysts and carriers were determined in an adsorption apparatus incorporating a McBain quartz-spring balance, adsorption isotherms being determined for benzene at 0°. The surfaces of the substances were first freed from adsorbed gases by exposure to a high vacuum ($10^{-5}-10^{-6}$ mm) at 250°. The distribution of pore size with respect to radius was calculated from the desorption branch of the isotherm with the aid of the Thomson-Kelvin formula [24],

$$RT \ln \frac{P_s}{P} = \frac{2\sigma V_m}{r},$$

($\frac{P}{P_s}$ is the relative pressure, σ is the surface tension of liquid benzene at 0°, V_m is the molar volume of liquid benzene, and r is the pore radius).

The results obtained are given in Table 2.

It follows from Table 2 that 1) the silica gel carrier has a greater specific surface and finer porous structure than the alumina; 2) the deposition of small amounts of metal on alumina does not generally affect the extent of the surface of this carrier, and the deposition of a similar amount of metal on silica gel always causes a slight increase in surface; 3) the deposition of metal on silica gel does not affect the position of the maximum on the curve for the distribution of pore size according to radius, but the deposition of some metals (Pd and Rh) on alumina causes an appreciable shift in the direction of smaller radii; 4) the total amount of benzene adsorbed on the surface at saturation is less on all of the catalysts investigated than on the corresponding carriers.

Methylcyclohexane. The methylcyclohexane used in the investigation was prepared by the hydrogenation of toluene in presence of Raney nickel at 180° in an autoclave. After necessary purification it had b.p. 99.8-100.6° (corrected), n_D^{20} 1.4230, and d_4^{20} 0.7693.

TABLE 2

Specific Surfaces of Catalysts and Carriers

Catalyst or carrier	Specific surface (sq.m/ g)	Position of maximum pore size on size-distribution curve (A)	Range of pore radii (A)	Total amount of adsorbed benzene at $\frac{P}{P_s}=1$ (millimoles/ g)
SiO_2, clear.	195	15 and 31	12 − 32	4.50
SiO_2, translucent. . .	195	14	11 − 18	3.20
0.5% Pt − SiO_2	220	15	11 − 18	3.70
0.5% Pd − SiO_2	220	15	12 − 24	3.70
1.0% Ru − SiO_2	220	14	11 − 20	3.25
0.5% Rh − SiO_2	220	15	12 − 20	3.55
Al_2O_3.	90	42	20	5.80
0.5% Pt − Al_2O_3. . . .	70	43	18	5.10
0.5% Pd − Al_2O_3. . . .	90	32	18	5.10
1.0% Ru − Al_2O_3. . . .	90	39	18	5.50
0.5% Rh − Al_2O_3. . . .	85	35	18	5.25

TABLE 3

Properties of Methylcyclohexane Catalyzates Obtained in Experiments with Different Catalysts

Catalyst	Amount of substance taken (g)	Amount of catalyzate obtained (g)	Gas and losses		Properties of catalyzate			Composition of gas (%)	
			(g)	(%)	n_D^{20}	d_4^{20}	Content of aromatic hydrocarbons (toluene) (%)	H_2	C_nH_{2n+2}
Pt − Al_2O_3	154.0	145.6	8.6	5.5	1.4820	0.8467	82.1	100	−
Pd − Al_2O_3	224.2	214.3	9.9	4.4	1.4820	0.8466	82.1	100	−
Rh − Al_2O_3	153.0	148.6	5.3	3.4	1.4537	0.8090	47.0	100	−
Ru − Al_2O_3	166.2	141.3	25.0	15.1	1.4425	0.7940	25.0	87	13
Pt − SiO_2	231.0	209.9	21.1	8.7	1.4937	0.8623	96.3	100	−
Pd − SiO_2	228.1	211.2	17.0	7.4	1.4910	0.8601	93.0	100	−
Rh − SiO_2	349.3	250.4	99.0	28.3	1.4620	0.8210	57.7	67.6	22.4
Ru − SiO_2	307.8	169.2	138.6	45.0	1.4264	0.7723	5.3	47.5	52.5

Apparatus and Procedure. The apparatus is described in a previous communication [25]. The experiments were carried out at 460° in presence of hydrogen at 20 atm pressure at a space velocity of 1.1 liters of methylcyclohexane per liter of catalyst, the ratio of hydrocarbon to hydrogen being 1 : 5. In addition, experiments with platinized alumina were carried out at 35 and 50 atm. The volume of catalyst was 50 ml in all experiments.

Investigation of Catalyzates. The methylcyclohexane catalyzates were investigated by the methods of precise rectification, chromatographic adsorption, and Raman spectra. Gaseous products were analyzed in an Orsat-Lunge apparatus.

The properties of the methylcyclohexane catalyzates obtained with various catalysts are given in Table 3, from which it can be seen that platinum and palladium, both on alumina and on silica, are extremely active catalysts for the reactions of methylcyclohexane. The least active catalyst is ruthenium on a silica carrier. The values given in Table 3 for the toluene contents (% by weight) of the catalyzates were determined from the data of Lozovoi and coworkers [26].

Aromatic hydrocarbons, which were separated from the catalyzates by adsorption on silica gel, were fractionated through a 33-plate column. Their fractional compositions and properties are given in Table 4.

The data in Table 4 show that the main direction of the transformations of methylcyclohexane under the given conditions is dehydrogenation to toluene. However, in addition to toluene, benzene and xylene were always found in the aromatic part of the catalyzate. From the catalyzate obtained in presence of rhodium on silica gel, 32.3% of benzene was isolated. Some fractions having boiling points below and above that of toluene were analyzed with the aid of Raman spectra. In the experiments with Pt−Al_2O_3, Pt − SiO_2, Pd − Al_2O_3, Pd − SiO_2, Rh − Al_2O_3

and Rh – SiO_2, the catalyzates contained small amounts (0.5-2.0%) of xylene. In the catalyzates obtained in presence of Pd – Al_2O_3, Pd – SiO_2, Pt – SiO_2 and Ru – SiO_2, 1.2-5% of benzene was found. Under the given conditions, therefore, demethylation and methylation processes occur.

TABLE 4

Fractional Composition and Properties of Aromatic Hydrocarbons isolated from Methylcyclohexane Catalyzates

Catalyst	Amount of aromatic hydrocarbons taken for fractionation (g)	Fraction	Properties of fractions			Weight of fraction (g)	Yield (% by weight)	
			Boiling range (°C)	n_D^{20}	d_4^{20}		on mixture taken	on original methylcyclohexane
Pt – Al_2O_3	107.4	I	105 – 109.6	1.4950	0.8648	0.8	0.74	68.2
		II	109.6 – 110	1.4968	0.8662	100.3	93.3	
		III	110 – 126	1.4973	0.8669	4.5	4.2	
			Residue			1.6	1.5	
Pd – Al_2O_3	156.0	I	104 – 109.7	1.4960	0.8646	3.5	2.2	68.7
		II	109.7 – 110.8	1.4958	0.8667	146.3	93.6	
		III	110.8 – 124	1.4969	0.8671	4.2	2.7	
			Residue			2.0	1.3	
Rh – Al_2O_3	40.7	I	107.5 – 109.5	1.4940	0.8629	0.6	1.4	25.1
		II	109.5 – 110.6	1.4970	0.8676	35.5	85.8	
		III	110.6 – 118	1.4970	0.8666	3.6	8.85	
			Residue			1.0	2.4	
Ru – Al_2O_3	31.2	I	106.5 – 109	1.4675	–	0.86	2.8	17.5
		II	109 – 110	1.4960	0.8660	26.2	84.0	
		III	110 – 110.5	1.4970	0.8663	2.5	8.0	
			Residue			1.7	–	
Pt – SiO_2	177.5	I	104 – 109	1.4980	0.8685	4.2	2.4	75.9
		II	109 – 110.5	1.4965	0.8684	168.0	94.7	
		III	110.5 – 125	1.4990	0.8698	3.0	1.7	
			Residue			2.3	1.3	
Pd – SiO_2	167.0	I	100 – 109	1.4940	0.8581	3.6	2.1	72.3
		II	109 – 110	1.4955	0.8664	156.9	94.0	
		III	110 – 115	1.4970	0.8669	4.3	2.6	
			Residue			2.2	1.3	
Rh – SiO_2	80.0	I	76.5 – 79.5	1.4860	–	0.8	1.0	22.3
		II	79.5 – 79.7	1.4995	0.8750	25.8	32.3	
		III	79.7 – 109	1.4970	0.8668	1.4	1.75	
		IV	109 – 110	1.4960	0.8655	45.0	56.3	
		V	110 – 130	1.5005	0.8713	3.3	4.1	
			Residue			1.6	2.0	
Ru – SiO_2	6.9		95 – 113°	1.4950	0.8649	6.5	94.2	2.1
			Residue			0.4	5.8	

The fractional composition and properties of the naphthene part of the methylcyclohexane catalyzate, which remains after chromatographic separation of the aromatic hydrocarbons, are shown in Table 5, from which it will be seen that the boiling points and other properties of the hydrocarbons isolated are considerably different from those of the original methylcyclohexane. In order to determine the composition of the mixture of hydrocarbons obtained we usedthe Raman-spectra method. The results of this investigation are given in Table 6, which shows that the main products of the transformations of methylcyclohexane are 1,2- and 1,3-dimethylcyclopentanes. In the presence of Pt – Al_2O_3 and of Pd – Al_2O_3 the main product of the transformations of methylcyclohexane is trans-1,2-dimethylcyclopentane. In presence of Rh – Al_2O_3 and Ru – Al_2O_3, in addition to 1,2-dimethylcyclopentane, appreciable amounts of 1,3-dimethylcyclopentane are formed in cis and trans forms. Also, a small amount of cyclohexane is present in almost all of the catalyzates.

TABLE 5

Fractional Composition and Properties of the Naphthene Parts of Methylcyclohexane Catalyzates

Catalyst	Amount of catalyst taken for fractionation (g)	Fraction	Properties of fractions			Weight of fraction (g)	Yield (% by weight)		
			Boiling range (°C)	n_D^{20}	d_4^{20}		on mixture taken	on catalyzate	on original methylcyclohexane
Pt − Al_2O_3	20.8	I	87 − 98	1.4168	0.7570	4.5	21.6	3.1	1.9
		II	98−100.5	1.4230	0.7688	8.6	41.4	5.9	5.6
		III	98−100.9	1.4233	0.7689	6.3	30.3	4.3	4.1
		Residue	−	−	−	1.4	6.7	−	−
Pd − Al_2O_3	44.5	I	85−98	1.4163	0.7564	5.5	12.3	2.6	2.5
		II	98−100.5	1.4230	0.7691	26.1	58.0	12.2	11.6
		III	98−100.5	1.4230	0.7690	10.4	24.5	4.9	46
		Residue	−	−	−	2.5	5.6	1.2	1.1
Rh − Al_2O_3	22.1	I	81 − 95	1.4110	0.7476	11.0	50.0	7.4	7.2
		II	95−100	1.4203	0.7624	4.2	19.1	2.8	2.7
		III	100−101	1.4235	0.7691	5.7	24.1	3.9	3.7
		Residue	−	−	−	1.2	5.5	0.8	0.3
Ru − Al_2O_3	69.0	I	84.5−91.0	1.4112	0.7482	10.0	14.5	7.1	6.0
		II	91.0−99.5	1.4200	0.7622	3.8	5.7	2.7	2.3
		III	99.5−100.5	1.4233	0.7693	46.4	67.3	32.9	28.0
		IV	100.5−103.0	1.4235	0.7702	6.3	9.2	4.5	3.8
		Residue	−	−	−	2.3	3.3	1.6	1.4
Pt − SiO_2	2.8	I	91.3−100.4	1.4186	0.7580	2.6	93.0	1.3	1.1
Pd − SiO_2	3.8	I	93−100.2	1.4190	0.7640	3.5	92.2	1.7	1.5
Rh − SiO_2	86.6	I	42−99.5	1.4155	0.7345	4.85	5.6	1.9	1.4
		II	99−100.5	1.4232	0.7697	70.0	81.0	28.0	20.1
		III	100.5−102.0	1.4235	0.7695	10.8	12.5	4.3	3.1
		Residue	−	−	−	1.0	1.2	0.4	0.3
Ru − SiO_2	161.5	I	95.6−99.5	1.4213	0.7643	10.0	6.2	5.9	3.3
		II	99.5−100.4	1.4232	0.7695	137.8	85.0	81.7	44.8
		III	100.4−103	1.4235	0.7696	9.2	5.7	5.5	3.0
		Residue	−	−	−	4.5	2.8	2.7	1.5

Transformations of Methylcyclohexane in presence of Alumina and Silica

In connection with these results it was of interest to determine the behavior of methylcyclohexane in presence of pure alumina and pure silica, such as we had used as carriers in the preparation of the catalysts. With this object we carried out catalysis experiments with methylcyclohexane over silica and over alumina in presence of hydrogen at 20, 35, and 50 atm, other experimental conditions being identical with those described above.

Analysis of the resulting catalyzates showed that under the given conditions both silica gel and alumina promote partial isomerization of methylcyclohexane into trans- and cis-1,2-dimethylcyclopentanes; with silica gel, however, this process occurs already at 20 atm, whereas with alumina isomerization is not appreciable until 50 atm is reached. Traces of cyclohexane were also found in the catalyzates, which points to partial demethylation of the original methylcyclohexane. It appears that cleavage of methylcyclohexane and its isomerization products does not occur in this case. Also, no aromatic hydrocarbons were detected in the catalyzates.

Effect of the Pressure of Hydrogen on the Degree of Conversion of Methylcyclohexane

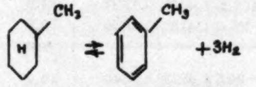
It was important to investigate in further experiments the effect of the pressure of hydrogen on the reactions of methylcyclohexane, other conditions being kept as before. The catalyst selected for this purpose was platinized alumina. We had already carried out experiments at 20 atm, and we now supplemented these by experiments at 35 and 50 atm.

TABLE 6

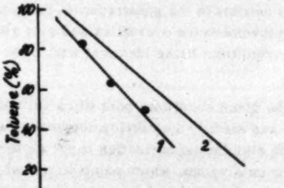
Results of the Optical Investigation of Methylcyclohexane Catalyzates

Catalyst	Fraction (see Table 5)	Composition (%)						
		trans-1,2-dimethylcyclopentane	cis-1,2-dimethylcyclopentane	trans-1,3-dimethylcyclopentane	cis-1,3-dimethylcyclopentane	cyclohexane	methylcyclohexane	cyclopentane
Pt–Al_2O_3	I	17–20	–	–	–	1.0–1.5	82–80	–
	II	6–7	–	–	–	–	94–93	–
	III	0.5	–	–	–	–	99.5	–
Pd–Al_2O_3	I	20–22	–	–	–	3	70–75	–
	II	8–10	–	–	–	–	90–92	–
	III	8–10	–	–	–	–	90–92	–
Rh–Al_2O_3	I	30	–	22	46	–	2–3	–
	II	23–20	–	–	–	–	77–80	–
	III	1	–	–	–	–	99	–
Ru–Al_2O_3	I	28	–	32	40	–	traces	–
	II	25	5	25	40	–	5	–
	IV	7–10	–	–	traces	traces	90–93	–
Rh–SiO_2	I	–	–	–	–	3.5	94	2.5
Ru–SiO_2	I	–	–	–	–	2–3	97	–

The graph gives the dependence of the yield of toluene on the pressure of hydrogen for a temperature of 460°, and also the yields of toluene calculated from Vvedensky's data [27] for the equilibrium concentrations in the following reaction at the same temperature: methylcyclohexane ⇌ toluene + hydrogen. At 50 atm the experimental values differ from the calculated values by 17 – 18%, whereas at lower pressures this difference falls to 8-5%. These discrepancies are to be explained by the fact that at higher pressure the reaction

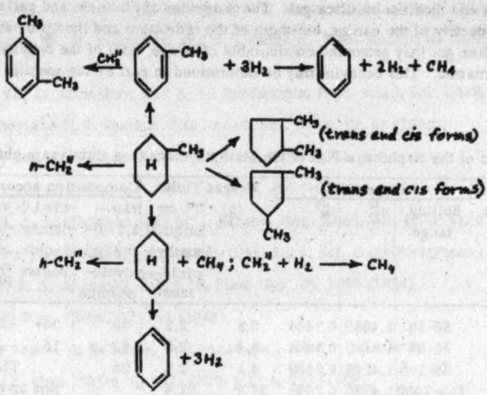


does not attain equilibrium owing to simultaneous isomerization of the methylcyclohexane into dimethylcyclopentanes. Optical analysis of fractions of the catalyzate shows that they contain more than 10% of dimethylcyclopentanes (on the original methylcyclohexane). Analysis of the aromatic hydrocarbons obtained showed that they consisted mainly of toluene, though 1-2% of m-xylene was present in the fraction boiling above 110°.



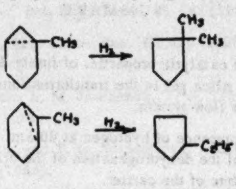
Dependence of the yield of toluene on the pressure of hydrogen (in experiments at 460°): 1-experimental data; 2-from equilibrium concentrations.

The experimental material that we have obtained relating to the transformations of methylcyclohexane in presence of platinum, palladium, rhodium, and ruthenium deposited on alumina and silica shows that this hydrocarbon undergoes various far-reaching changes under the given conditions. The reactions that occur may be expressed as follows:



The main reaction of methylcyclohexane under the given conditions is its dehydrogenation to toluene. The amounts of benzene and xylenes present in the catalyzates are very small. Only in experiments with the rhodium-silica catalyst was there a considerable amount of benzene (32%) in the aromatic part of the catalyzate. Under the given conditions, therefore, the processes of demethylation and methylation of the benzene nucleus occur, with participation of methylene radicals [20-22]. Under our conditions the source of methylene radicals may be the methylene breakdown of the original methylcyclohexane and of other cycloalkanes formed from it by hydrogenolysis of the side group (cyclohexane) or by isomerization with contraction of the ring (dimethylcyclopentanes).

Another important reaction is the isomerization of methylcyclohexane into dimethylcyclopentanes. In the catalyzates we found 1,2- and 1,3-dimethylcyclopentanes. With one exception ($Pt-Al_2O_3$ at 35 atm) we could not detect the presence of 1,1-dimethylcyclopentane and ethylcyclopentane in the catalyzates, although these substances could be formed from methylcyclohexane by ring contraction according to the schemes:



However, in the catalysis experiment on methylcyclohexane in presence of $Pt-Al_2O_3$ at 460° and 35 atm we detected the presence of about 34% of 1,1-dimethylcyclopentane in the 86-90° fraction of the catalyzate by the optical method (Table 7). We intend to investigate this interesting observation in greater detail in the future.

It is interesting that under the given conditions in presence of silica gel or alumina methylcyicohexane undergoes partial isomerization to dimethylcyclopentanes. The literature shows that at 450° in absence of pressure, neither over alumina [28, 29], nor over silica [28] does the cyclohexane ring suffer any appreciable change. Under the same conditions cyclohexene and 4-methylcyclohexene are isomerized in presence of alumina [28] and of silica [28] into the corresponding dimethylcyclopentenes.

In 1943 Haensel and Ipatieff [30], in a study of the reactions of cyclohexane over alumina at 570-578° in presence of hydrogen at 100 atm in a flow system, showed that under these conditions cyclohexane is partially isomerized into methylcyclopentane. A similar observation was made earlier by Ipatyev (Ipatieff) and Dovgelevich [29]. With respect to the dehydrogenation of methylcyclohexane, platinum and palladium had practically the same, high activity under the given conditions; rhodium was more active than ruthenium. Platinum, palladium, and rhodium were more active when carried by silica gel than when carried by alumina. Ruthenium, on the other hand, was more active on alumina. The most active catalysts in effecting the far-reaching breakdown of the hydrocarbons were ruthenium and rhodium on silica gel. The properties of platinum and palladium catalysts were not greatly dependent on the identity of the carrier, but those of the ruthenium and rhodium catalysts were. When these were deposited on silica gel they promoted considerable cleavage, both of the original hydrocarbon and of the products of its transformation. This behavior may be determined in part by the specific surfaces of the carriers (see above).

TABLE 7

Composition and Properties of the Naphthene Part of the Methylcyclohexane Catalyzate obtained over Pt–Al_2O_3

Pressure of hydrogen (atm)	Amount of substance (g)	Fraction	Properties			Weight (g)	Yield (% on original methylcyclopentane	Composition according to optical analysis (%)					
			Boiling range (°C)	n_D^{20}	d_4^{20}			trans-1,2-dimethylcyclopentane	cis-1,2-dimethylcyclopentane	trans-1,3-dimethylcyclopentane	cis-1,2-dimethylcyclopentane	methylcyclopentane	cyclohexane
35	57.2	I	86-90	1.4085	0.7404	3.8	2.2	30	34•	22	11	–	3
		II	90-95	1.4115	0.7464	4.4	2.8	60	15	12	8	4	–
		III	95-100	1.4205	0.7639	4.1	2.5	25		Traces	–	75	–
		IV	100-100.2	1.4235	0.7695	34.3	21.4		Not investigated				
		V	100.2-102	1.4235	0.7698	9.6	6.3		Not investigated				
		Residue		–	–	0.4							
50	65	I	84-90	1.4113	0.7451	6.6	4.6	25	8	22	45	–	–
		II	90-95	1.4123	0.7488	7.1	5.0	30	–	22	46	2	–
		III	95-99	1.4213	0.7646	6.1	4.3	Traces	–	–	–	100	–
		IV	99-99.5	1.4230	0.7694	38.8	27.3	Not investigated					
		V	99.5-102.0	1.4235	0.7695	3.1	2.2	Traces	–	–	–	100	–
		Residue		–	–	2.7							

• 1,1-Dimethylcyclopentane

SUMMARY

1. An investigation was made of the catalytic properties of finely dispersed platinum, palladium, rhodium, and ruthenium deposited on alumina and on silica gel in the transformations of methylcyclohexane at 460° in presence of hydrogen at 20, 35, and 50 atm in a flow system.

2. It was shown that at 460° and in presence of hydrogen at 20 atm the main reaction of methylcyclohexane is dehydrogenation to toluene. The extent of the dehydrogenation of the original hydrocarbon depends both on the nature of the metal and on the chemical nature of the carrier.

3. It was shown that under the given conditions dehydrogenation is accompanied by isomerization processes with formation of isomeric dimethylcyclopentanes and also by the demethylation and methylation of hydrocarbons with participation of methylene radicals.

4. With increase in pressure, other conditions being maintained constant, there is an increase also in the extent to which methylcyclohexane undergoes isomerization with contraction of the ring.

5. Study of the behavior of methylcyclohexane in contact with silica and alumina showed that these oxides promote partial isomerization of the original hydrocarbon into dimethylcyclopentanes.

LITERATURE CITED

[1] N. D. Zelinsky, Selected Works, Vol. I and II, Acad. Sci. USSR Press, Moscow and Leningrad, 1941.

[2] S. Yu. Elovich and G. M. Zhabrova, Theoretical Principles of the Hydrogenation of Fats, Acad. Sci. USSR Press, Moscow, 1948.

[3] S. N. Obryadchikov, Petroleum Technology. Part 2, Moscow and Leningrad, 1952, p. 305.

[4] A. M. Rubinshtein, Kh. M. Minachev, and N. I. Shuikin, Proc. Acad. Sci. USSR, 62, 497 (1948); 67, 287 (1949).

[5] N. I. Shuikin, Kh. M. Minachev, and A. M. Rubinshtein, Proc. Acad. Sci. USSR, 79, 89 (1951).

[6] Kh. M. Minachev and N. I. Shuikin, Proc. Acad. Sci. USSR, 72, 61 (1950).

[7] B. A. Kazansky and A. F. Plate, J. Gen. Chem. 7, 328 (1937).

[8] B. A. Kazansky and A. F. Plate, J. Gen. Chem. 9, 496 (1939).

[9] B. A. Kazansky, A. L. Liberman, and M. I. Batuev, Proc. Acad. Sci. USSR 41, 67(1948).

[10] A. F. Plate, Catalytic Aromatization of Paraffins, Acad. Sci. USSR Press, Moscow and Leningrad, 1948.

[11] N. D. Zelinsky, B. A. Kazansky, and A. F. Plate, Ber. 68, 1869 (1936).

[12] B. A. Kazansky, Prog. Chem. 17, 641 (1948).

[13] N. D. Zelinsky and A. A. Balandin, Bull. Acad. Sci. USSR 7, 29 (1929).

[14] A. A. Balandin Z. phys. Chem. 3, 167, 1929; ibid 4, 289 (1929).

[15] A. A. Balandin, Jubilee Collection, dedicated to the Thirtieth Anniversary of the Great October Socialist Revolution, Moscow and Leningrad, 1947, p. 627.

[16] V. Haensel, Oil and Gas J. 48, 82 (1950).

[17] V. Haensel, Petr. Process 5, 356 (1950).

[18] M. L. Kastens and R. E. Sutherland, Ind. Eng. Chem. 42, 582 (1950).

[19] V. Haensel and G. R. Donaldson, Ind. Eng. Chem. 43, 2102 (1951).

[20] N. I. Shuikin, N. G. Berdnikova, and S. S. Novikov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, No. 2, 269.*

[21] N. I. Shuikin, S. S. Novikov, and N. G. Berdnikova, Proc. Acad. Sci. USSR 89, 1029 (1953).

[22] N. D. Zelinsky and N. I. Shuikin, Proc. Acad. Sci. USSR 3, No. 4, 255 (1934).

[23] F. G. Ciapetta and I. B. Hunter, Ind. Eng. Chem. 45, 147 (1953).

[24] J. W. McBain, A. M. Baker, J. Am. Chem. Soc. 48, 690 (1926); A. V. Kiselev, Prog. Chem. 14, 367 (1945).

[25] Kh. M. Minachev, N. I. Shuikin, L. M. Feofanova, T. G. Treshchova and T. P. Yudkina, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No. 6, 1067.

[26] A. V. Lozovoi, M. K. Dyakova, and T. G. Stepantseva, J. Gen. Chem. 7, 1119 (1937); A. A. Balandin and N. I. Shuikin, J. Phys. Chem. 5, 707 (1934).

[27] A. A. Vvedensky, Thermodynamical Calculations for Processes of the Fuel Industry, State Fuel Tech. Press, Leningrad and Moscow, 1949.

[28] Yu. A. Arbuzov, Sci. Mem. Moscow State Univ. 89, 70 (1945).

[29] V. N. Ipatyev and P. Dovgelevich, J. Russ. Phys. Chem. Soc. 43, 1431 (1911).

[30] V. Haensel and V. N. Ipatieff, Ind. Eng. Chem. 35, 632 (1943).

Received May 12, 1954

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

---

* Consultant's Bureau Translation, p 243.

BLANK
PAGE

DESTRUCTIVE ALKYLATION OF BENZENE WITH PENTANE

I. M. Tolchinsky, B. A. Krentsel, and A. V. Topchiev

Investigation of the thermal and catalytic processes occurring in the transformations of pure hydrocarbons and mixtures of hydrocarbons under various conditions is of undoubted interest for the extension of our ideas concerning the chemistry and mechanisms of the complex reactions occurring in thermocatalytic treatments of petroleum. Not only the many thermocatalytic transformations of hydrocarbons, but also the destructive alkylation of aromatic hydrocarbons with paraffins is deserving of attention. As is well known, in this process cracking of the paraffin molecule is associated with the simultaneous addition of the resulting unsaturated hydrocarbon to the thermally more stable molecule of benzene or other aromatic hydrocarbon.

The general equation for the destructive alkylation of aromatic hydrocarbons with paraffins is as follows:

$$C_{(m+n)}H_{2(m+n)+2} + ArH \longrightarrow C_nH_{2n+2} + ArC_mH_{2m+1}$$

In the literature various catalysts have been proposed for the destructive alkylation of aromatic hydrocarbons. In the alkylation of benzene with 2,2,4-trimethylpentane [1] the following catalysts were tried: aluminum chloride, zirconium chloride, boron trifluoride, and magnesium chloride. Aluminum and zirconium chlorides were active catalysts; in presence of boron trifluoride and magnesium chloride the reaction did not go. The product of the reaction was tert-butylbenzene, and the further alkylation of this yield di-tert-butylbenzene.

Other authors have investigated the destructive alkylation of benzene with hexane and with 2,2,4-trimethylpentane in presence of orthophosphoric acid [2]. The amount of catalyst taken was about 20% of the total amount of reactants. Treatment of a mixture of benzene and hexane at 450° for ten hours in a revolving autoclave gave a yield of liquid reaction products amounting to 84% of the weight of starting materials, and the gas formed amounted to 6 liters from every 100 g of reacting hydrocarbons. The liquid products contained 2.8% of isopropylbenzene and 7.1% of butylbenzenes, the remainder being unchanged benzene and hexane. The gas contained 54% of ethane, 28% of hydrogen, and 18% of propane. In the reaction with 2,2,4-trimethylpentane tert-butylbenzene was formed, as in the experiment in presence of aluminum chloride; the gaseous products contained 63.2% of isobutane.

In a patent [3] it is proposed to carry out the alkylation of aromatic hydrocarbons by means of paraffins in presence of an aluminosilicate catalyst at about 450°. No information is given about the conditions of the process and the composition of the products.

The literature on the reaction of paraffins with benzene is therefore almost entirely concerned with the investigation of reactions occurring in presence of metal chlorides and phosphoric acid. It was considered to be of interest to study the reactions of benzene with the lower paraffins in presence of a technical aluminosilicate catalyst under conditions close to those that we used previously in our investigations of the thermal transformations of pentane [4].

EXPERIMENTAL

The starting materials were a pentane fraction obtained by the rectification of a light straight-run gasoline and commercial benzene, which was distilled and collected within a range of 1°. The characteristics of these materials are given in Table 1.

The reactions were carried out in a 500-ml rotating autoclave. The procedure was the same as that used in the investigation of the transformations of pentane [4]. The liquid reaction products were fractionated, the fractions collected being: up to 60°, 60-95°, 95-122°, 122-150°, 150-200°, and above 200°. The fractions boiling above 95° were regarded as the actual reaction products. These fractions were then subjected to precise rectification through a column having a metal packing and equivalent in resolving power to fifty theoretical plates. The narrow fractions obtained by precise rectification were characterized by the usual physicochemical properties, and some of them were investigated with the aid of their Raman spectra. In experiments directed to the study of the overall balance sheet of the reaction, the gaseous products were collected and analyzed in a low-temperature rectification apparatus.

TABLE 1

Characteristics of Starting Materials

Substance	d_4^{20}	n_D^{20}	Boiling range	Bromine number
Pentane	0.6297	1.3579	34-36.3	0
Benzene	0.8798	1.5009	79-80	–

Effect of Temperature, Duration of Reaction, and Amount of Catalyst on the Yield of Products formed in the Reaction of Pentane with Benzene

a) Effect of Temperature. Experiments to determine the effect of temperature on the yields of products were carried out with equimolecular amounts of benzene and pentane; the duration of reaction was 120 minutes, and the amount of catalyst (commercial aluminosilicate catalyst in spherical granules) was 23-25% on the weight of reacting hydrocarbons. The results of typical experiments of this series are given in Table 2.

Analysis of the results in Table 2, which are represented graphically in Fig. 1, shows that, as the temperature is raised, the yield of gas increases at the expense of a reduction in the amount of liquid reaction products. This conclusion is in accord with results that we obtained in a study of the autodestructive alkylation of pentane over an aluminosilicate catalyst. Control experiments carried out under the same conditions with benzene alone (no pentane) showed that benzene underwent no appreciable change. In view of the above considerations, it is not advisable to carry out the reaction at above 450-460°.

TABLE 2

Effect of Temperature on the Yields of Products of the Destructives Alkylation of Benzene with Pentane

Amount taken (g)		Experimental conditions				Yields of reaction products (% by weight)			Yield of fractions boiling above 95° (% by weight)		d_4^{20} of liquid reaction products
C_6H_6	C_5H_{12}	Temperature (°C)		pressure (atm)		gas	liquid	coke + losses	on liquid product	on starting materials	
		maximum	average	maximum	average						
122	113	450	455	520	425	22.7	66.5	10.8	56.0	31.7	0.7573
137	126	440	435	570	530	13.0	65.0	22.0	44.7	29.2	0.7836
137	126	425	420	430	420	3.8	80.5	15.7	35.4	28.6	0.7568
145	133	398	390	530	515	0.36	88.5	11.14	9.35	8.3	0.7460

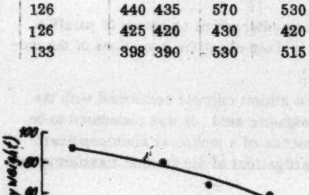


Fig. 1 (based on Table 2). The effect of temperature on the yield of liquid products of the alkylation of benzene with pentane (duration of experiment 120 minutes; amount of catalyst 23.5-26.6% by weight).
Curve 1-The whole liquid product; Curve 2-fraction boiling above 95°, calculated on liquid product; Curve 3 - fraction boiling above 95°, calculated on starting materials.

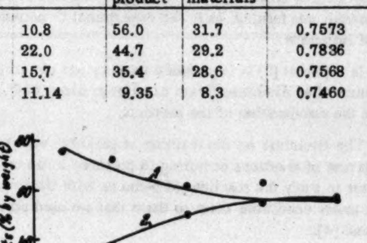


Fig. 2. (based on Table 3). The effect of duration of contact on the yield of liquid products of the destructive alkylation of benzene with pentane.
Curve 1- The whole liquid product; Curve 2-fraction boiling above 95°, calculated on the starting materials; Curve 3-fraction boiling above 95°, calculated on the liquid.

b) Effect of the Duration of Reaction. The experiments on the effect of the duration of reaction on the yields of the products of the reaction of benzene with pentane were carried out with the same amounts of reactants and catalyst. The results are given in Table 3 and are represented graphically in Fig. 2.

Analysis of the results in Table 3 shows that increase in the duration of the reaction to more than 60 minutes does not lead to an appreciable increase in the yield of products boiling above 95°, i.e. products of the interaction of benzene and pentane.

c) Effect of the Amount of Catalyst. Experiments to determine the effect of the amount of catalyst were carried out at about 450° for a contact time of 10 minutes. The results given in Table 4 show that increase in the amount of catalyst to above 12% (on the reactants) had almost no effect, over the investigated range, on the yields of gas and liquid reaction products.

TABLE 3

Effect of Duration of Contact on the Yields of the Products of the Destructive Alkylation of Benzene with Pentane

Amount taken (g)		Experimental conditions				Duration of reaction (in minutes)	Yields of reaction products (% by weight)			Yield of fractions boiling above 95° (% by weight)		d_4^{20} of crude product
C_6H_6	C_5H_{12}	Temperature (°C)		pressure (atm)			gas	liquid	coke + losses	on liquid product	on starting materials	
		maximum	average	maximum	average							
127	118	465	462	490	480	10	6.5	75.5	18	30.3	22.9	0.7644
124	115	460	455	490	445	30	12.2	72.3	15.5	38.3	27.8	0.8019
119	111	460	455	518	459	60	18.3	61.0	20.7	49.4	30.0	0.8267
118	109	460	455	448	380	90	16.8	62.5	20.9	55.5	34.8	—
122	113	460	455	520	425	120	22.7	56.5	20.8	56.0	31.7	0.7573

TABLE 4

Effect of Amount of Catalyst on the Yields of Products

Amount taken (g)		Experimental conditions				Yields of reaction products (% by weight)			Yield of fractions boiling above 95° (% by weight)		d_4^{20} of reaction products	Amount of catalyst (% by weight on reactants)
C_6H_6	C_5H_{12}	Temperature (°C)		pressure (atm)		gas	liquid	coke	on liquid product	on starting materials		
		maximum	average	maximum	average							
115	108	470	465	440	418	9.65	61.5	29.0	32.8	20.2	0.7718	58.8
124	116	470	468	555	522	7.3	69.0	24.0	35.0	24.2	0.7727	45.8
132	123	465	462	535	525	7.0	75.5	18.5	28.6	21.6	0.7660	26.3
127	118	465	462	425	425	5.8	84.3	9.7	27.5	23.2	0.7729	14.3
135	125	465	462	530	520	6.4	82.8	10.9	28.0	23.1	0.7655	12.7
137	128	470	460	490	457	6.1	86.8	7.15	10.45	9.05	0.7603	0.0
119•	111	470	460	490	395	21.4	63.0	15.5	20.7	13.0	0.8549	0.0

• Duration of contact 120 minutes.

However, in absence of catalyst reaction proceeds with a considerably lower yield of liquid product. Results given in this table are represented also in Fig. 3.

Investigation of Liquid Reaction Products obtained in the Reaction of Pentane with Benzene

The amount of liquid products taken for investigation was 2000 ml (it had been previously distilled, to remove unchanged pentane, from a flask fitted with a dephlegmator), and this was fractionated through a column of high productivity (the load in the flask was 2000 ml) having a metal packing equivalent in resolvability to thirty theoretical plates. The following wide fractions were obtained:

Frac. I,	up to	40°;	114 ml;	5.7%
Frac. II,	b.p.	40-95°;	1173 ml;	58.4%
Frac. III,	b.p.	95-200°;	570 ml;	28.7%
Frac. IV,	b.p.	> 200°;	63 ml;	3.2%
		Losses —	80 ml;	4.0%

Fraction I, which came over below 40°, had the following characteristics: d_4^{20} 0.6301; n_D^{20} 1.3587, bromine number 0, amount of sulfonatables 0. This fraction, therefore, was unchanged pentane. Fraction II was refractionated through the same column into narrower fractions. The results of this fractionation are given in Table 5.

TABLE 5

Results of Fractionation of the Fraction boiling at 40-95°

Fraction	Boiling range (°C)	Yield (%) by volume	n_D^{20}	d_4^{20}	Notes
I	33.4-42.4	6.1	1.3600	0.6301	8.4% of the
II	43 - 60.0	0.9	1.3802	0.6698	losses in frac-
III	60.4-73.0	10.8	1.4695	—	tionation are
IV	73.0-77.0		1.4722	—	added to the
V	79.4-79.9	82.8	1.4998	—	first two frac-
VI	Residue				tions
	> 80°	17.2	—	—	

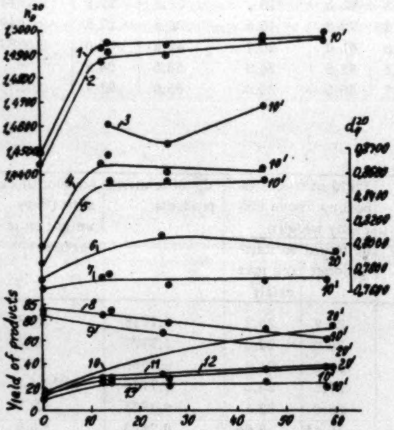


Fig. 4. Fractionation of the 95-300° fraction of the liquid product (see Table 7) of the destructive alkylation of benzene with pentane. Curves: 1) densities of fractions from secondary fractionation; 2) refractive i indices of fractions from secondary fractionation; 3) secondary fractionation of the 95-200° fraction (section AB); 4) primary fractionation.

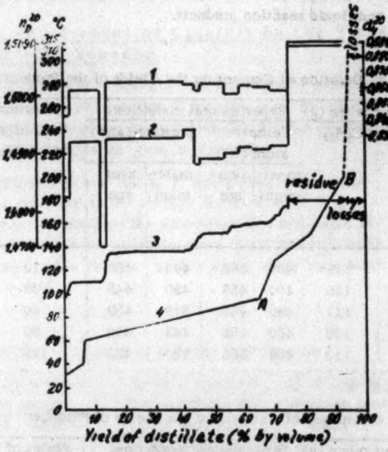


Fig. 3. Effect of amount of catalyst on yield of liquid reaction products; Expt. conditions: 460-470°, 420-520 atm, 10 and 20 minutes. Curves: 1) n_D^{20} fraction (150-200°); 2) n_D^{20} fraction (95-150°); 3) n_D^{20} "crude" product; 4) denstiy, fraction (150-200°); 5) density, fraction (95-105°); 6) density, "crude" liquid product; 7)-density, "crude" liquid product; 8) of whole liquid product; 9) of the whole liquid product; 10) of fraction boiling 95°, on liquid product; 11) of fraction boiling 95°, on reactants; 12) of fraction boiling 95°, on liquid product; 13) of fraction boiling 95°, on reactants

As the properties cited show, these fractions (64% of sulfonatables) consisted mainly of unchanged benzene, and they also contained products of the autodestructive alkylation of pentane. These fractions were not investigated in greater detail.

The fraction boiling at 95-200° was fractionated into three fractions with the properties set forth in Table 6.

In order to characterize the composition of this wide fraction in greater detail we carried out its precise rectification through a 50-plate column. Before rectification this fraction was treated at 0° with three portions (each 10% by volume) of 86% sulfuric acid. The product was was washed with caustic soda solution and with water, distilled over sodium, and dried over calcined calcium chloride; 97.5% of the original amount then remained. After this treatment the product had the following properties: n_D^{20} 1.4935, d_4^{20} 0.8639, amount of sulfonatables (by means of Kattwinkel's mixture) 96%, and bromine number 0.84.

The results of the rectification of 250 ml of the fraction are given in Table 7 and represented graphically in Fig. 4.

TABLE 6

Fraction	Boiling range (°C)	Amount (%)	n_D^{20}	d_4^{20}	Molecular weight	Bromine number	Amount of sulfonatables (% by weight)
I	95-122	17.8	1.4894	0.8573	115	1.36	88.4
II	122-150	42.2	1.4909	0.8564	108	1.42	95.0
III	150-200	40.0	1.4948	0.8658	124	2.03	95.1

TABLE 7

Results of the Precise Rectification of the Fraction Boiling at 95-200°

Fraction	Boiling range	Yield (% by volume)		n_D^{20}	d_4^{20}	Molecular weight	Bromine number	Amount of sulfonatables (%)
		actual	cummulative					
I	95-109.0	1.8	1.8	1.4825	0.8431	–	–	–
II	109.5-111.0	10.2	12.0	1.4920	0.8597	94.0	–	96
III	111.3-128.0	2.0	14.0	1.4740	0.8313	–	–	–
IV	132.8-136.5	26.0	40.0	1.4925	0.8630	104	–	95.9
V	137.4-141.5	2.8	42.8	1.4941	0.8620	105	–	97.6
VI	140-148.5	2.6	45.4	1.4881	0.8578	109	–	88.6
VII	150.5-152.0	8.4	53.8	1.4890	0.8627	118	–	76.0
VIII	157 - 157.2	4.6	58.4	1.4900	0.8562	123	0.03	97.5
IX	158.5-159.8	4.4	62.8	1.4919	0.8614	122	0.0	97.6
X	160.3-162.0	5.8	68.6	1.4906	0.8605	117	0.0	82.0
XI	162.7-174.7	6.0	74.6	1.4912	0.8580	125	0.8	63.7
XII	>174.7	18.6	93.2	1.5082	0.8898	–	–	–
XIII	Losses	6.8	100.0	–	–	–	–	–

The residue in the flask (XII), amounting to 45 ml, was united with fractions boiling over the range 200-300° from all experiments, amounting to 72 ml, and the mixture was fractionated through a column. The results of this fractionation are given in Table 8.

TABLE 8

Results of Fractionation of Residues

Boiling range (°C)	Yield (% by volume)	n_D^{20}	d_4^{20}	Molecular weight
177-181	11.1	1.4945	0.8668	131
181-183	15.4	1.4952	0.8737	136
183-191	23.0	1.4996	0.8755	138
191-201	38.4	1.5042	0.8796	138
201-209	43.2	1.5250	0.9109	143
233-255	73.5	1.5862	0.9931	152
255-274	92.0	1.5884	0.9928	162
274-292	100.0	1.5840	0.9902	176

The residues from the fractionations were not investigated in greater detail. The densities, molecular weights, and refractive indices indicate the presence of aromatic hydrocarbons of high molecular weight.

For some of the narrow fractions obtained in the rectification (95-200° fraction), the molecular refractions were calculated. The values obtained are given in Table 9.

Certain fractions were investigated in Prof. M. M. Kusakov's laboratory by the Raman-spectra method. The measurements were carried out by M. Serebrennikova, to whom we express our thanks. The results obtained in this spectrum investigation are given in Table 10.

The fraction boiling over the range 150.5-152.8°, in which the presence of ethylmethylbenzenes could be presumed, was oxidized by the usual alkaline permanganate procedure. The acid so obtained did not melt below 300°, but sublimed. Elementary analysis of the acid gave the following results:

	%C	%H	%O
Found	57.62	3.80	38.6
	58.24	3.93	38.6
Calculated for phthalic acid	57.2	3.62	38.58

TABLE 9

Identification of the Narrow Fractions of the Product from their Molecular Refractions

Fraction	Boiling range	Supposed hydrocarbon	MR		Amount of sulfonatables	Purity of product (according to MR)
			Found	Calculated		
II	109.5-111.0	Toluene	31.8	30.925	96	97.5
IV	132.8-136.5	Ethylbenzene	35.1	35.543	95.9	98.7
V	137.4-141.5	Xylenes	35.6	36.643	97.6	97.5
VI	140 - 148.5	o-Xylene	37.9	36.643	88.6	96.5
VII	150.5-152.0	Isopropylbenzene	40.9	40.161	76.0	98.5
VIII	157 - 157.2	Propylbenzene	41.5	40.161	97.5	97.0
IX	158.5-159.8	1-Ethyl-3-methylbenzene	41.5	40.161	97.6	97.0
X	160.3-162.0	1-Ethyl-4-methylbenzene	39.4	40.161	82.0	98.0

TABLE 10

Results of the Spectrum Analysis of some of the Narrow Fractions

Fraction	Boiling range (°C)	n_D^{20}	d_4^{20}	Composition of fraction
IV	132.8-136.5	1.4925	0.8630	Consists mainly of ethylbenzene; traces of m-xylene were detected, and slight traces of ethylcyclohexane may be present
V	137.4-141.5	1.4941	0.8620	Consists of ethylbenzene and m-xylene in the proportions of 3 : 1; some p-xylene and traces of o-xylene are present
VI	140 -148.5	1.4881	0.8378	Contains o-xylene with some m- and p-xylenes, and isopropylbenzene with some ethyl- and propyl-benzenes
VII	150 - 152	1.4890	1.8627	Contains isopropylbenzene with some propylbenzene

A sample of the acid (0.6458 g) was treated with 46 ml of methanol saturated with hydrogen chloride in a water bath for six hours. Water was then added, and a white mass of crystals came down. The yield of dry product after recrystallization from pentane was 0.4707 g. The crystals melted at 60°. The reported melting point of dimethyl isophthalate is 67-68°. Elementary analysis of dimethyl isophthalate:

	%C	%H	%O
Found	62.76	5.00	32.24
	62.68	5.20	32.12
Calculated for dimethyl phthalate	61.80	5.15	33.05

The results obtained by the oxidation of the investigated fraction confirm that it consisted essentially of ethylmethylbenzene.

The results that we have described prove fairly conclusively that the products of the reaction of pentane with benzene over an aluminosilicate catalyst under the given conditions are toluene, ethylbenzene, isomeric xylenes, isopropylbenzene, and other alkylated aromatic hydrocarbons.

Composition of the Gaseous Reaction Products

The gas formed in the interaction of benzene with pentane was fractionated in a low-temperature rectification apparatus (TsIATIM-51) and shown to contain the components listed in Table 11*.

---

* The analysis was carried out in the gas laboratory by Z. Nechaeva.

The analysis of the gas taken in conjunction with the results of the investigation of the liquid products enables us to form some views concerning the chemistry of the processes occurring in the course of the interaction of benzene with pentane.

TABLE 11

Analysis of the Gas

Component	Content (% by volume)	Notes
Hydrogen	8.2	The sp.gr. of the gas was about 1.0
Methane	33.0	
Ethane	40.5	
Propane	12.8	
Isobutane	2.0	
Residue	3.5	

We have previously shown [4] that in the thermal and thermocatalytic transformations of pentane in presence of an aluminosilicate catalyst the pentane undergoes destructive alkylation, which is preceded by the cracking of pentane, occurring, for example, according to the following equations:

$$C_5H_{12} \longrightarrow C_2H_4 + C_3H_8;$$

$$C_5H_{12} \longrightarrow C_4H_8 + CH_4;$$

$$C_5H_{12} \longrightarrow C_3H_6 + C_2H_6.$$

When benzene is present in the reaction mixture, the unsaturated hydrocarbons formed in this way may react with it with formation of the corresponding alkylbenzenes:

$$C_6H_6 + C_2H_4 \rightarrow C_6H_5C_2H_5;$$

$$C_6H_6 + C_3H_6 \rightarrow C_6H_5C_3H_7 \text{ etc.}$$

Determinations of the free energy changes for some "overall" reactions of benzene and pentane show that they are all thermodynamically possible under the temperature conditions of our experiments. The presence of ethane, propane, and butane in the gaseous reaction products supports the view that the above reactions occur. The possibility is not excluded of the occurrence also of breakdown of pentane into free radicals, e.g. $C_5H_{12} \rightarrow C_3H_7 +$ $+ C_2H_5$ or $C_5H_{12} \rightarrow C_5H_{11} + H$, and subsequent reaction of the free radicals with benzene.

It is noteworthy that in the reactions of pentane with benzene, but not in the earlier experiments on the autodestructive alkylation of pentane, the yield of the fraction boiling above 95° depends greatly on whether catalyst is present. This fact is probably associated with the directive influence of the aluminosilicate catalyst on the alkylation of benzene with the unsaturated hydrocarbons formed by the breakdown of the pentane. The primary act – the breakdown of the pentane – goes to approximately the same extent both in presence of aluminosilicate catalyst, and in its absence; but the secondary process – alkylation of benzene by unsaturated hydrocarbons – is accelerated by an aluminosilicate catalyst. The effects of other homogeneous and heterogeneous catalysts on the reaction of benzene with pentane are deserving of special study.

SUMMARY

1. The destructive alkylation of benzene with pentane over an aluminosilicate catalyst under autoclave conditions was effected for the first time.

2. The effects of the duration of reaction, temperature, and amount of catalyst on the yield of reaction products were investigated.

3. It was shown that destructive alkylation of benzene with an equimolecular amount of pentane under autoclave conditions results in the formation of a mixture of alkylated aromatic hydrocarbons (in an amount equal to 34% by weight of the original mixture) together with gaseous hydrocarbons (23% by weight on the original mixture).

4. The alkylated aromatic hydrocarbons obtained in the autoclave experiments were investigated, and it was shown that they included toluene, ethylbenzene, isopropylbenzene, xylenes, and ethylmethylbenzene. The gaseous reaction products were investigated and it was shown that they consisted mainly of saturated hydrocarbons.

LITERATURE CITED

[1] A. V. Grosse and V. N. Ipatyev, J. Gen. Chem 6, 1514 (1936).

[2] V. N. Ipatieff, V. Y. Komarewsky, H. Pines, J. Am. Chem. Soc. 58, 918 (1936).

[3] A. Sachanen, S. Davis, U. S. Patent 2234984.

[4] A. V. Topchiev, Ya. M. Paushkin, B. A. Krentsel, and I. M. Tolchinsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, No. 2, 260* (See Consultant's Bureau Translation, p237.)

Received July 20, 1954

Petroleum Institute of the USSR Academy of Sciences

BLANK
PAGE

BEHAVIOR OF 3-, 4-, AND 5-ALKENYL HALIDES IN CONDENSATION REACTIONS WITH ALKYL HALIDES IN PRESENCE OF MAGNESIUM

M. A. Cheltsova, E. A. Chernyshev, and A. D. Petrov

It is known that the condensation reactions of allyl and 2-methylallyl halides with Grignard reagents derived from primary, secondary, and tertiary alkyl halides give high yields and so provide a convenient method for the synthesis of hydrocarbons. Whereas the presence of a double bond in the β-position with respect to halogen (2-alkenyl halides) results in greatly increased activity, as compared with the corresponding saturated alkyl halide, a double bond in the α-position (1-alkenyl halide) completely deactivates the halogen compound. We have recently shown that a double bond in the γ-position has a similar effect [1].

It was of great interest to determine whether this alternation of activity and inactivity continued further, i.e. in the 4- and 5-alkenyl halides. The present investigation was undertaken with the object of resolving this question, and in it we have confirmed the complete inactivity of 3-alkenyl halides, on the basis of new examples, and have shown that 4-alkenyl halides differ greatly from 2-alkenyl halides, their activities being only about 50% of those of the corresponding alkyl halides. Finally, it was found that a 5-alkenyl halide is active, but its activity is very little different from that of the corresponding alkyl halide. It was thus shown that the alternation of inactivity and enhanced activity in alkenyl halides is interrupted already when the double bond is in the δ-position (4-alkenyl halide), the activity then being not higher, as might be expected, but lower than that of the corresponding alkyl halide. In the 5-alkenyl halides, owing to the remoteness of the double bond with respect to the halogen the mutual effect of this bond and the halogen already approaches zero, and in activity this unsaturated halogen compound differs little from the corresponding saturated compound.

Condensation of Methylmagnesium Bromide with Tertiary 3-, 4-, and 5-Alkenyl Halides

We have shown previously that, whereas methylmagnesium bromide readily condenses with dimethylpropylmethyl chloride (2-chloro-2-methylpentane) with formation of 2,2-dimethylpentane, this reagent does not react with allyldimethylmethyl chloride (4-chloro-4-methyl-1-pentene) with formation of 4,4-dimethyl-1-pentene [1]. The inertness of 3-alkenyl halides was shown also by examples of the behavior of secondary and primary 3-alkenyl halides. In continuation of this work, in the present investigation we have shown that even when the double bond is tertiary, as in 4-bromo-2,4-dimethyl-1-pentene, the 3-alkenyl bromide does not condense with methylmagnesium bromide. The same is true of 4-bromo-4-phenyl-1-pentene.

4-Alkenyl halides were found to be quite different in reactivity. 5-Chloro-5-methyl-1-hexene condensed with methylmagnesium bromide with formation of 5,5-dimethyl-1-hexene in 10% yield. It is true that, in condensing with methylmagnesium bromide, 2-chloro-2-methylhexane formed 2,2-dimethylhexane in 20% yield, so that introduction of the δ-double bond reduced the yield, though not to zero as did the introduction of a γ-double bond in the tertiary alkyl halide of analogous structure. It is interesting that, contrary to expectation, the condensation of 5-bromo-5-methyl-1-hexene with $CH_2=CH-CH_2MgBr$ gave not a higher, but a lower yield than the corresponding reaction with CH_3MgBr. Ozonization of the resulting 4,4-dimethyl-1,7-octadiene showed that some 4,4-dimethyl-2,6-octadiene was present as impurity.

If double bonds can migrate into mutually closer positions during the condensation of alkenyl halides, then the possibility cannot be excluded of a partial migration of the double bond from the δ- to the γ-position in the original 5-bromo-5-methyl-1-hexene, and this could explain the relatively low yield of condensation products from 4-alkenyl halides and also the lower yield obtained from $CH_2=CH-CH_2MgBr$ than from CH_3MgBr. By the condensation of 6-bromo-6-methyl-1-heptene with methylmagnesium bromide a 13% yield of the previously undescribed 6,6-dimethyl-1-heptene was obtained. It is evident, therefore, that a double bond in the 5-position with respect to the halogen no longer has any effect on the activity.

Condensation of a Grignard Reagent derived from a Primary 3-Alkenyl Halide with Tertiary Alkyl Halides

We have shown previously [1] that 3-butenylmagnesium bromide does not react with tributylmethyl chloride

(5-butyl-5-chlorononane), whereas under the same conditions butylmagnesium bromide reacts with this chloro compound with formation of tetrabutylmethane (5,5-dibutylnonane) in 15% yield. In continuation of these experiments we have shown in the present investigation that a primary normal 4-alkenyl halide, unlike the analogous 3-alkenyl halide, will condense not only with 5-butyl-5-chlorononane, but also with tripropylmethyl chloride (4-chloro-4-propylheptane) and with trimethylmethyl chloride (2-chloro-2-methylpropane). Yields varied from 6 to 12%, i.e. were somewhat less than those of the C_{12}-C_{19} tetraalkylmethanes synthesized by us previously [2] by the condensation of 5-butyl-5-chlorononane and 4-chloro-4-propylheptane with primary alkyl halides under similar conditions in presence of mercuric chloride.

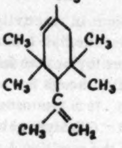
EXPERIMENTAL

1. Reaction of Allylmethylphenylmethyl Bromide (4-Bromo-4-phenyl-1-pentene) with CH_3MgBr. The reaction, like that of this reagent with 4-halo-4-methyl-1-pentenes, did not go. The only substance isolated was the product of the hydrolysis of the original bromo compound, allylmethylphenylmethanol (2-phenyl-4-penten-2-ol).

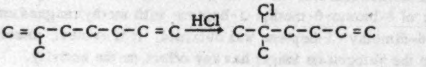
2. Reaction of 4-Bromo-2,3-dimethyl-1-pentene with CH_3MgBr. 2,4-Dimethyl-4-penten-2-ol was prepared from 2-methylallyl chloride and acetone by Yarovsky's method in 46% yield. Altogether 300 g of the alcohol was prepared, and this by treatment with phosphorus tribromide gave a 23.5% yield of 4-bromo-2,4-dimethyl-1-pentene; b.p. 50-52° (30 mm); n_D^{20} 1.4645; d_4^{20} 1.1450; Found MR 42.73; Calculated MR 41.83. When this bromo compound (86 g) was added to excess of methylmagnesium bromide there was a rise in temperature. When the addition was complete, the mixture was heated in a water bath. The greater part of the ether was distilled off, and the mixture was again heated at 60-70° for ten hours. Fractional distillation yielded the following three fractions:

Frac. I,	b.p.	80-83°;	n_D^{20} 1.4170;	10 g	
Frac. II,	b.p.	97-100°;	n_D^{20} 1.4220; d_4^{20} 0.7287;	3 g	
Frac.III,	b.p.	213-215°;	n_D^{20} 1.4785;	16.5 g;	yield 33.5%

Fractions I and II were identified as mixtures of 2,4-dimethyl-1,3-pentadiene and 2,4-dimethyl-1,4-pentadiene, and they contained traces of a 2,4,4-trimethylpentene (probably 2,4,4-trimethyl-2-pentene) as indicated by the Raman spectrum (the frequency 756 cm^{-1}). Fraction III consisted of the cyclic dimer of 2,4-dimethylpentadiene. The presence of a tertiary carbon atom and of two double bonds was indicated by the frequencies: 373, 343, 575, 766, 905, 927, 935, 1125, 1150, 1266, 1304, 1356, 1377, 1427, 1628, 1641, 1677, 2998 cm^{-1}. In the ozonization products formic acid and a nonvolatile acid, giving a silver salt containing 31.16% Ag, were detected. It is probable that the hydrocarbon was identical with the cyclic dimer of 2,4-dimethyl-1,3-pentadiene prepared by Merezhkovsky [1]. Oxidation of this hydrocarbon should yield a diketo acid giving a silver salt containing 30.95% Ag.



3. Reaction of 5-Chloro-5-methyl-1-hexene with CH_3MgBr and of 5-Bromo-5-methyl-1-hexene with $CH_2=CH-CH_2MgBr$. 5-Chloro-5-methyl-1-hexene was synthesized from 2-methyl-1,5-hexadiene, which was prepared by Yarovsky's method by addition of a mixture of 2-methylallyl chloride and allyl bromide to magnesium. 2-Methyl-1,5-hexadiene had b.p. 86-88°; d_4^{20} 0.7257; n_D^{20} 1.4180; Found MR 33.7; Calculated MR 33.59; it was obtained in 30% yield.

Addition of HCl according to the scheme 

$$C=\underset{C}{C}-C-C-C-C=C \xrightarrow{HCl} C-\overset{Cl}{\underset{C}{C}}-C-C-C-C=C$$

gave a 50% yield of 5-chloro-5-methyl-1-hexene, b.p. 131-132° (748 mm); n_D^{20} 1.4330; d_4^{20} 0.8842; Found MR 38.95; Calculated MR 38.93; Found 26.99% Cl; Calculated for $C_7H_{13}Cl$ 26.79% Cl; Calculated M 132.5; Calculated M 130.5.

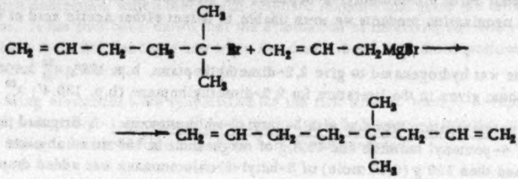
By condensation of 132 g of 5-chloro-5-methyl-1-hexene with methylmagnesium bromide 11 g (10%) of 5,5-dimethyl-1-hexene was obtained; it had b.p. 100-102°; n_D^{20} 1.4030; d_4^{20} 0.7136; Found MR 38.80; Calculated MR 38.68.

The synthesis of 5-bromo-5-methyl-1-hexene was carried out by the same route; it had b.p. 87-89° (95 mm); d_4^{20} 1.1664; n_D^{20} 1.4605; Found MR 41.59; Calculated for $C_7H_{13}Br$ MR 41.82.

Found %: C 47.57; H 7.60; Br 45.08

$C_7H_{13}Br$. Calculated %: C 47.45; H 7.41; Br 45.14

The bromo compound (330 g) was added to allylmagnesium bromide prepared from 400 g of allyl bromide. The mixture was heated in a water bath for 20 hours, and then, after removal of ether, it was heated at 80-90° for ten hours. The product was 12.4 g of 4,4-dimethyl-1,7-octadiene, formed as follows:



$$CH_2=CH-CH_2-CH_2-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Br + CH_2=CH-CH_2MgBr \longrightarrow$$

$$\longrightarrow CH_2=CH-CH_2-CH_2-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-CH=CH_2$$

The yield was thus only 5%. The substance had b.p. 145-148°; d_4^{20} 0.7647; n_D^{20} 1.4330; Found M 138.4; calculated M 138.1

Found %: C 86.0; H 13.88

$C_{10}H_{18}$. Calculated %: C 86.55; H 13.05

The 4,4-dimethyl-1,7-octadiene was hydrogenated to 4,4-dimethyloctane, b.p. 152-154°; n_D^{20} 1.4132; d_4^{20} 0.7225; Found MR 49.09; calculated MR 49.38. The frequencies 756, 913, 931, 1196, and 1231 cm^{-1} in the Raman spectrum confirmed the presence of a quaternary carbon in the middle of the chain of this hydrocarbon.

4,4-Dimethyl-1,7-octadiene was ozonized. The products identified were formic acid (calomel), acetic acid (silver salt containing 64.64% Ag), and dimethylsuccinic acid, m.p. 137°; found M 153.2; calculated M 146; found 59.92% Ag; calculated 59.96% Ag. 3,3-Dimethylhexanedioic acid was also identified; found 55.17% Ag, calculated 55.50% Ag.

The frequencies 769, 912, 937, 1196, 1235 and 750, 910, 930, 1200, 1250 cm^{-1} in the Raman spectrum confirmed the presence of a quaternary carbon atom and of two double bonds at the extreme ends of the chain, but there was also a small amount of a hydrocarbon having double bonds in the two penultimate positions. It follows, therefore, both from the oxidation results and from the spectra, that the 4,4-dimethyl-1,7-octadiene was associated with some 4,4-dimethyl-2,6-octadiene. The lowness of the yield of the required diene prompted us to identify the remaining products; it was found that there was 50% of unchanged bromo compound (5-bromo-5-methyl-1-hexene) and 30% of the diolefin resulting from its dehydrohalogenation.

4. Reaction of 6-Bromo-6-methyl-1-heptene with CH_3MgBr. The starting material for the preparation of 6-bromo-6-methyl-1-heptene was 2-furaldehyde, which was hydrogenated at 150° under an initial pressure of 100 atm: 2600 g of 2-furaldehyde yielded 1900 g of tetrahydrofurfuryl alcohol, b.p. 170-175°. From this alcohol 520 g of tetrahydrofurfuryl bromide was prepared by the action of phosphorus tribromide. Tetrahydrofurfuryl bromide was converted into 4-penten-1-ol, from which 572 g of 5-bromo-1-pentene, b.p. 125-126°, was obtained. From 5-bromo-1-pentene, as its Grignard reagent, and acetone 2-methyl-6-hepten-2-ol was prepared as follows. The Grignard reagent was prepared from 149 g (1 mole) of 5-bromo-1-pentene and 24 g of magnesium, and 45 g (0.8 mole) of acetone was added at 0°. The mixture was heated in a water bath, cooled, and decomposed with 10% acetic acid. The experiment was repeated several times, and 572 g of 5-bromo-1-pentene gave 304 g of 2-methyl-6-hepten-2-ol, b.p. 162° (756 mm); n_D^{20} 1.4380; d_4^{20} 0.8423; found MR 39.93; calculated for $C_8H_{16}O$ MR 40.20; found (by Tserevitinov's method) OH 12.20%; calculated OH 13.20%.

6-Bromo-6-methyl-1-heptene was prepared as follows. A mixture of 154 g of 2-methyl-6-hepten-2-ol and 20 g of dry pyridine was added gradually at − 5° to 110 g of freshly distilled phosphorus tribromide. From the resulting mixture, 115 g of a bromo compound boiling at 65-66° (20 mm) was isolated. The experiment was repeated, and altogether 230 g of the bromo compound was obtained; it had d_4^{20} 1.1163; n_D^{20} 1.4640; found MR 47.24; for $C_8H_{15}Br$ calculated MR 46.23. When 114 g (0.6 mole) of 6-bromo-6-methyl-1-heptene was added to methylmagnesium bromide prepared from 36 g (1.5 moles) of magnesium, no rise in temperature was observed. When the whole of the bromo compound had been added, the reaction mixture was heated for ten hours, after which the greater part of the ether was removed and the mixture was again heated for ten hours at 60-70°. The experiment was repeated. Fractionation through an 18-plate column yielded 20 g (10%) of a product having b.p. 128-130°; n_D^{20} 1.4220; d_4^{20} 0.7465; found MR 42.94; calculated for C_9H_{18} MR 43.30; iodine number found 205; calculated 202; found: 85.80% C; 14.22% H; calculated for C_9H_{18} 85.62% C; 14.38% H.

The presence of the frequencies 1645, 2998, and 1296 cm^{-1} in the Raman spectrum indicated that the hydrocarbon contained a tertiary carbon atom and a double bond, mainly terminal, but to some extent also in the penultimate position. Ozonization yielded formic acid and an acid of m.p. 34° and molecular weight 144.5. Analysis of the silver salt gave 43.35% Ag. Dimethylhexanoic acid $C_8H_{16}O_2$ has a molecular weight of 144.23 and its silver salt contains 42.96% Ag. The hydrocarbon obtained, therefore, was the previously undescribed 6,6-dimethyl-1-heptene in admixture with about 5% of 6,6-dimethyl-2-heptene, the presence of which was established only by the optical method (among the ozonization products we were unable to detect either acetic acid or dimethylvaleric acid).

6,6-Dimethyl-1-heptene was hydrogenated to give 2,2-dimethylheptane, b.p. 128°, n_D^{20} 1.4030; d_4^{20} 0.7157, these constants being close to those given in the literature for 2,2-dimethylheptane (b.p. 130.4°; n_D^{20} 1.4024; d_4^{20} 0.7105).

5. Reaction of 4-Pentenylmagnesium Bromide with 5-Butyl-5-chlorononane. A Grignard reagent was prepared from 80 g (0.54 mole) of 4-pentenyl bromide and 12.8 g of magnesium in 150 ml of absolute ether, 5 g of mercuric chloride was added, and then 100 g (0.46 mole) of 5-butyl-5-chlorononane was added dropwise at 15-25° over a period of five hours. After the whole of the chlorocompound had been added, stirring was continued for three hours, and the mixture was then heated at the boiling point of ether for a further three hours. A voluminous white precipitate was formed. The mixture was stirred at room temperature for about 20 hours and was then decomposed with water and 10% hydrochloric acid. The ether layer was washed with weak sodium carbonate solution and with water, united with the ether extract, and dried over calcium chloride. The ether was distilled off, and the residue was vacuum-fractionated. The fractionation yielded 67.6 g of the dehydrochlorination product 5-butyl-4-nonene, b.p. 90-93° (10 mm) and n_D^{20} 1.4369; 3.8 g of a fraction boiling at 93-139° (10 mm), and 6.9 g of 6,6-dibutyl-1-decene, b.p. 139-141° (10 mm); n_D^{20} 1.4480; d_4^{20} 0.7987; found MR 84.83; calculated MR 85.00; yield 6.1%.

Found %: C 85.75; 85.82; H 14.28; 14.34
$C_{18}H_{36}$. Calculated %: C 85.62; H 14.38

6. Reaction of 4-Pentenylmagnesium Bromide with 4-Chloro-4-propylheptane. The reactants were 74.5 g (0.5 mole) of 4-pentenyl bromide, 12 g (0.5 mole) of magnesium, and 70.5 g (0.4 mole) of 4-chloro-4-propylheptane. The procedure and conditions were as in the previous experiment. After the necessary treatment the ether was distilled off and the residue was vacuum-fractionated. The fractionation yielded 43.6 g of the dehydrochlorination product 4-propyl-3-heptene, b.p. 62-65° (20 mm) and n_D^{20} 1.4348, 2.3 g of a fraction boiling at 64-123° (20 mm), and 7.1 g (8.4%) of 6,6-dipropyl-1-nonene, b.p. 123-125° (20 mm); n_D^{20} 1.4408; d_4^{20} 0.7825; calculated MR 71.11; found MR 70.98.

Found %: C 85.52; 85.74; H 14.28; 14.30
$C_{15}H_{30}$. Calculated %: C 85.62; H 14.38

7. Reaction of 4-Pentenylmagnesium Bromide with tert-Butyl Chloride. The reaction was carried out by the same procedure and under the same conditions as the reaction described in Section 5. During the reaction isobutene gas was evolved. The substances taken for reaction were 149 g (1 mole) of 4-pentenyl bromide, 24 g of magnesium, and 73.5 g (0.8 mole) of tert-butyl chloride. Fractionation through an 18-plate column yielded 8.6 g of 2,4,4-trimethyl-2-pentene, b.p. 101-105.5°, n_D^{20} 1.4108; d_4^{20} 0.7186, and 11.7 g (11.7%) of 6,6-dimethyl-1-heptene, b.p. 125.5-126.5° (758 mm); n_D^{20} 1.4212; d_4^{20} 0.7395; calculated MR 43.33; found MR 43.16.

Found %: C 85.72; 85.78; H 14.30; 14.28
C_9H_{18}. Calculated %: C 85.63; H 14.37

We express our deep gratitude to M. I Batuev, who carried out the spectrum analysis of the hydrocarbons that we prepared.

SUMMARY

1. In a study of the reactions of methylmagnesium bromide with 4-bromo-4-phenyl-1-pentene and with 4-bromo-2,4-dimethyl-1-pentene we have obtained further confirmation of the inactivity in condensation reactions of alkenyl halides having a γ-double bond.

2. In a study of the condensations of 5-chloro-5-methyl-1-hexene with methylmagnesium bromide, of 5-bromo-5-methyl-1-hexene with allylmagnesium bromide, and of 4-pentenylmagnesium bromide with 5-butyl-5-chlorononane, with 4-chloro-4-propylheptane, and with 2-chloro-2-methylpropane, we have shown that alkenyl halides having a δ-double bond, both tertiary and primary, condense with formation of olefins in a yield that is only about 50% of that obtained in the corresponding reactions with the corresponding alkyl halides.

3. Taking the condensation of 6-bromo-6-methyl-1-heptene with methylmagnesium bromide as example, we have shown that a double bond in the ε-position with respect to the halogen has no longer any effect on the activity of the halogen compound, which reacts with Grignard reagents and gives the same yields as the corresponding alkyl halides. It has thus been shown that the alternation of inactivity (α- and γ-double bonds) with activity (very high for a β-double bond and low when the double bond is in the δ-position) is interrupted when the double bond reaches the δ-position.

4. The following substances were synthesized for the first time: 2-methyl-6-hepten-2-ol, 6-bromo-6-methyl-1-heptene, 6,6-dimethyl-1-heptene (by two methods), 6,6-dipropyl-1-nonene, and 6,6-dibutyl-1-decene. Raman spectra have been determined for some of the compounds prepared.

Received May 8, 1954

N. D. Zelinsky Institute of Organic Chemistry of the
USSR Academy of Sciences

LITERATURE CITED

[1] A. D. Petrov, M. A. Cheltsova, and E. A. Chernyshev, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, No. 6, 1087.*

[2] A. D. Petrov and E. A. Chernyshev, Proc. Acad. Sci. USSR 86, No. 5, 957 (1952).

---

* Consultant's Bureau Translation, p 949.

BLANK
PAGE

SYNTHESIS OF ORGANOSILICON ESTERS OF PROPIONIC AND ISOBUTYRIC ACIDS, AND THEIR PROPERTIES

D. N. Andreev, B. N. Dolgov, and E. V. Kukharskaya

Organosilicon esters derived from alkylsilanes have not yet received adequate study. The compounds described in the literature are mainly acetoxysilanes in which silicon is attached to alkyl [1-4], alkenyl [5], chloroalkyl [6], or aryl [7] radicals. Very few organosilicon esters of monobasic acids higher than acetic are known [8, 9]. In particular, practically no derivatives of propionic and isobutyric acids have been described. Only four such compounds are known: tetrakis(propionyloxy)silane [10], tetrakis(butyryloxy)silane [11], and ethyltris- and diethylbis-(propionyloxy) silanes, which were described in a patent [12].

We now describe the synthesis and properties of twelve organosilicon esters of propionic and isobutyric acids, of which ten have been prepared for the first time. They are derivatives of methyl- and ethyl-silanes in which various numbers of alkyl and acyloxy groups are attached to silicon. They were prepared by the reaction of alkylchlorosilanes with sodium salts of the acids [2] according to the equation:

$$R_{4-x}SiCl_x + x\,NaOOCR' \longrightarrow R_{4-x}Si(OOCR')_x + xNaCl.$$

The esters so obtained are clear colorless liquids that are readily hydrolyzed by water. As the number of acyloxy groups attached to silicon increases, the rate of hydrolysis also increases. One result of this was that we were unable to determine the molecular weights of alkyltris(acyloxy)silanes. The densities of the synthesized esters increase in regular manner as the methyl or ethyl radicals are replaced by acyloxy groups. The refractive index varies as follows: replacement of methyl by acyloxy results in a regular rise in refractive index, but replacement of ethyl by the same acyloxy groups results in a slight fall in refractive index.

TABLE 1

No.	Ester	Formula	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	M		MR		Yield (%)
						found	calculated	found	calculated	
I	Trimethyl(propionyloxy)silane......	$(CH_3)_3SiOOCC_2H_5$	122-123 (757)	0.8614	1.3931	147	146.23	40.51	40.30	41.1
II	Dimethylbis(propionyloxy)silane....	$(CH_3)_2Si(OOCC_2H_5)_2$	83.5-84 (10)	1.0057	1.4086	197	204.26	50.17	50.32	61.7
III	Methyltris(propionyloxy)silane.......	$CH_3Si(OOCC_2H_5)_3$	139 (15)	1.0939	1.4140	–	262.30	59.91	50.34	50.9
IV	Triethyl(propionyloxy)silane.......	$(C_2H_5)SiOOCC_2H_5$	83-85 (14)	0.8885	1.4202	183	188.31	53.66	54.19	63.8
V	Diethylbis(propionyloxy) silane ..	$(C_2H_5)_2Si(OOCC_2H_5)_2$	108.5-109.5(13)	0.9896	1.4193	232	232.32	59.32	59.58	45.9
VI	Ethyltris(propionyloxy)silane...	$C_2H_5Si(OOCC_2H_5)_3$	119 (5)	1.0660	1.4180	–	276.33	64.22	64.97	51.5
VII	(Isobutyryloxy)-trimethylsilane...	$(CH_3)_3SiOOCCH(CH_3)_2$	43.5-44 (20)	0.8501	1.3950	166	160.26	45.10	44.93	47.3
VIII	Bis(isobutyryloxy)-dimethylsilane....	$(CH_3)_2Si[OOCCH(CH_3)_2]_2$	95-95.5 (13)	0.9751	1.4057	234	232.32	59.35	59.58	72.9
IX	Tris(isobutyryloxy)-methylsilane.....	$CH_3Si[OOCCH(CH_3)_2]_3$	126-127 (12)	1.0223	1.4090	–	304.38	73.97	74.23	26.3
X	Triethyl(isobutyryloxy)silane.......	$(C_2H_5)_3SiOOCCH(CH_3)_2$	88 (14)	0.8743	1.4190	200	202.34	58.59	58.82	65.3
XI	Diethylbis(isobutyryloxy)silane.....	$(C_2H_5)_2Si[OOCCH(CH_3)_2]_2$	123-125 (19)	0.9538	1.4160	268	260.37	68.77	68.84	53.2
XII	Ethyltris(isobutyryloxy)silane......	$C_2H_5Si[OOCCH(CH_3)_2]_3$	129 (5)	1.0144	1.4140	–	318.41	78.81	78.86	35.9

EXPERIMENTAL

For all of the syntheses the procedure was as follows. The sodium salt of the acid (0.1-0.5 mole), which had been dried at 100-110° for four hours, was introduced into a round-bottomed flask fitted with reflux condenser, which was connected to a system of air driers, a mercury-sealed mechanical stirrer, and a dropping funnel. Dry petroleum ether (100-500 ml, freshly distilled over sodium) was added, and the mixture was stirred while a solution of one part of the alkylchlorosilane in one part of dry petroleum ether was added from the dropping funnel. Reaction occurred with evolution of heat. When the whole of the alkylchlorosilane had been added, the mixture was stirred at the boiling point of petroleum ether for 8-12 hours. When the mixture was cool, the liquid part was separated from the precipitate of salts by filtration through a sintered glass filter in an atmosphere of dry air. Petroleum ether was distilled off, and the reaction products were fractionated twice under reduced pressure in a current of dry air.

Constants of the synthesized esters are given in Table 1, and analytical data in Table 2. The yields given for the esters refer to the narrow fractions obtained after the second fractionation, which are described in the table. The molecular weights of the esters were determined cryoscopically in benzene, ester numbers were determined by hydryolsis of a weighed sample of the substance with a solution of caustic potash in ethylene glycol [13], and molecular refractions were calculated from Warrick's component values [14]. Silicon was determined in a weighed amount of ester by mineralization with a mixture of concentrated sulfuric and nitric acids. We did not succeed in determining silicon in (I), (II), (VII), and (VIII) by this method; for these we give the results of analysis for carbon and hydrogen.

TABLE 2

No.	Ester number		Amount Si (%)		Amount of C (%)		Amount of H (%)	
	found	calculated	found	calculated	found	calculated	found	calculated
I	379	383	–	–	46.69	49.27	9.89	9.65
II	541	549.3	–	–	47.14	47.03	7.88	7.89
III	650	642	10.72	10.69	–	–	–	–
IV	302	297	14.42	14.90	–	–	–	–
V	488	482	11.87	12.08	–	–	–	–
VI	618	609	9.93	10.15	–	–	–	–
VII	350	350	–	–	52.13	52.45	9.74	10.06
VIII	485	483	–	–	51.49	51.68	8.71	8.67
IX	577	552	9.32	9.22	–	–	–	–
X	277	277	13.48	13.86	–	–	–	–
XI	423	428	10.34	10.78	–	–	–	–
XII	528	526	8.97	8.81	–	–	–	–

SUMMARY

Twelve organosilicon esters, of which ten are here described for the first time, were synthesized by the action of methyl- and ethyl-chlorosilanes on the sodium salts of propionic and isobutyric acids.

LITERATURE CITED

[1] R. O. Sauer, W. J. Patnode, J. Am. Chem. Soc. 67, 1548 (1945).

[2] H. A. Schuyten, J. W. Weaver, J. D. Reid, J. Am. Chem. Soc. 69, 2110 (1947).

[3] R. O. Sauer, J. Am. Chem. Soc. 68, 138 (1946).

[4] K. A. Andrianov, A. A. Zhdanov, and A. A. Bogdanova, Proc. Acad. Sci. USSR 94, 697 (1954).

[5] K. C. Frisch, P. A. Goodwin, R. E. Scott, J. Am. Chem. Soc. 74, 4584 (1952).

[6] F. C. Boye, H. W. Post, J. Org. Chem. 17, 1386 (1952).

[7] N. S. Nametkin, A. V. Topchiev, and F. F. Machus, Proc. Acad. Sci. USSR 87, 233 (1952).

[8] D. N. Andreev and L. L. Shchukovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, No. 1, 135.*

---

* Consultant's Bureau Translation, p 121

[9] B. N. Dolgov, N. P. Kharitonov, and M. G. Voronkov, J. Gen. Chem. 24, No. 9, (1954).

[10] F. G. Launing, J. Am. Chem. Soc. 75, 1596 (1953).

[11] K. D. Petrov and M. I. Itkina, J. Gen. Chem. 17, 220 (1947).

[12] C. A. MacKenzie, M. Schoffman, U. S. Pat. 2537073 (9/1 1951); C. A. 45, 3410 (1951).

[13] L. N. Petrova and O. V. Shvarts, Analysis of Synthetic Perfumes, 1941, p. 65, Food Indust. Press.

[14] E. Warrick, J. Am. Chem. Soc. 68, 2455 (1946).

Received May 19, 1954

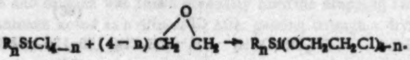
Institute of Silicate Chemistry of the USSR Academy
of Sciences

BLANK
PAGE

REACTIONS OF EPICHLOROHYDRIN AND OF GLYCIDOL WITH ORGANOCHLOROSILANES

K. A. Andrianov, N. N. Sokolov, E. N. Khrustaleva, and L. N. Yukina

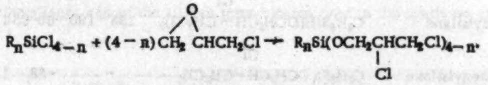
The reactions of α-epoxides with organohalosilanes have received little study. There are only two papers relating to the reactions of ethylene oxide with organochloro- and organobromo-silanes. In one of these [1] the products are described of the reaction of some organochlorosilanes with ethylene oxide according to the equation:



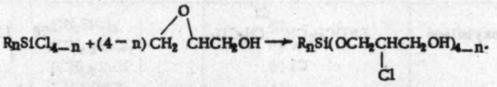
$$R_nSiCl_{4-n} + (4-n)\,CH_2\overset{O}{—}CH_2 \rightarrow R_nSi(OCH_2CH_2Cl)_{4-n}.$$

In the second paper [2] the reactions of tribromomethylsilane and dibromodimethylsilane with ethylene oxide are described. Reactions of epoxides with organohalosilanes are, however, of interest in that they enable Si − O − C links to be obtained without the elimination of hydrogen halide. This peculiar feature of these reactions is applied, for example, in the preparation of certain organic polysiloxanes [3] and in the resolution of azeotropes of organosilicon compounds [4].

We have studied the reactions of epichlorohydrin and of glycidol with organochlorosilanes, and have found that they proceed according to the equations:



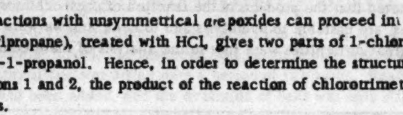
$$R_nSiCl_{4-n} + (4-n)\,CH_2\overset{O}{—}CHCH_2Cl \rightarrow R_nSi(OCH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2Cl)_{4-n}. \qquad (1)$$



$$R_nSiCl_{4-n} + (4-n)\,CH_2\overset{O}{—}CHCH_2OH \rightarrow R_nSi(OCH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2OH)_{4-n}. \qquad (2)$$

As a result of reactions proceeding according to Equation 1, we have prepared the compounds that are listed with their formulas and some of their properties in Table 1. Some compounds prepared according to Equation 2 are listed in Table 2. All of these reactions were exothermic, and the heat evolved was particularly great in the reactions with terfunctional organochlorosilanes. Also, it was found that the reactivity of the α-epoxy ring was so great that reaction of the hydroxyl of glycidol with the chlorine of the organochlorosilane either did not go, or went to only a slight extent. The compounds obtained readily underwent hydrolysis, especially in presence of hydrochloric acid.

It is known that reactions with unsymmetrical α-epoxides can proceed in two directions. Thus, isobutylene oxide (1,2-epoxy-2-methylpropane), treated with HCl, gives two parts of 1-chloro-2-methyl-2-propanol and one part of 2-chloro-2-methyl-1-propanol. Hence, in order to determine the structures of the compounds obtained in accordance with Equations 1 and 2, the product of the reaction of chlorotrimethylsilane and epichlorohydrin was submitted to hydrolysis.

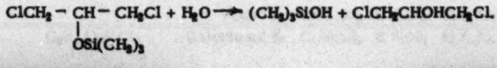


$$(CH_3)_3SiCl + CH_2\overset{O}{—}CHCH_2Cl \begin{cases} \rightarrow (CH_3)_3SiOCH_2CHClCH_2Cl & \text{(a)} \\ \rightarrow ClCH_2-\underset{\displaystyle OSi(CH_3)_3}{\underset{|}{CH}}\cdot CH_2Cl & \text{(b)} \end{cases} \qquad (3)$$

We showed that hydrolysis of the compounds formed according to Equation 3 yields the corresponding alkylsilanols and dichloropropanols. In the given case, hydrolysis of the product formed in accord with Equation 3 (a) would yield trimethylsilanol and 2,3-dichloro-1-propanol:

$$(CH_3)_3SiOCH_2CHClCH_2Cl + H_2O \rightarrow (CH_3)_3SiOH + HOCH_2CHCl\,CH_2Cl$$

The product formed by Equation 3 (b) would give trimethylsilanol and 1,3-dichloro-2-propanol:



$$ClCH_2-\underset{\displaystyle OSi(CH_3)_3}{\underset{|}{CH}}-CH_2Cl + H_2O \rightarrow (CH_3)_3SiOH + ClCH_2CHOHCH_2Cl.$$

TABLE 1

Substance (°C)	Formula	B.p. in °C (p in mm)	Freezing point	d_4^{20}	n_D^{20}	MR	
						found	calculated
Tris(2,3-dichloropropoxy)methylsilane	$CH_3Si(OCH_2-\underset{Cl}{CH}-CH_2Cl)_3$	–	−83−85	1.3452	1.4906	88.50	89.51
Bis(2,3-dichloropropoxy)dimethylsilane	$(CH_3)_2Si(OCH_2-\underset{Cl}{CH}-CH_2Cl)_2$	160−165 (37)	−93−97	1.2720	1.4772	64.80	69.70
(2,3-Dichloropropoxy)trimethylsilane	$(CH_3)_3Si(OCH_2-\underset{Cl}{CH}-CH_2Cl)$	96−100 (66)	−55−57	1.1094	1.4456	45.4	49.0
Bis(2,3-dichloropropoxy)methylsilane	$CH_3SiH(OCH_2-\underset{Cl}{CH}-CH_2Cl)_2$	173-175 (34)	−55−57	1.3740	1.4782	58.8	65.3
Tris(2,3-dichloropropoxy)ethylsilane	$C_2H_5Si(OCH_2-\underset{Cl}{CH}-CH_2Cl)_3$	–	−47	1.3740	1.4880	91.2	94.0
Bis(2,3-dichloropropoxy)diethylsilane	$(C_2H_5)_2Si(OCH_2-\underset{Cl}{CH}CH_2Cl)_2$	150−200 (36)	−89	–	1.4815	–	–
(2,3-Dichloropropoxy)triethylsilane	$(C_2H_5)_3Si(OCH_2-\underset{Cl}{CH}-CH_2Cl)$	65−70 (100)	−68	1.0776	1.4492	61.7	63.0
Bis(2,3-dichloropropoxy)ethylsilane	$C_2H_5SiH(OCH_2\underset{Cl}{CH}-CH_2Cl)_2$	185−190 (34)	−60−65	1.2992	1.4790	65.7	70.44
Tris(2,3-dichloropropoxy)phenylsilane	$C_6H_5Si(OCH_2\underset{Cl}{CH}-CH_2Cl)_3$	–	−68	1.3666	1.5247	106.10	107.61
Tetrakis(2,3-dichloropropoxy)silane	$Si(OCH_2\underset{Cl}{CH}-CH_2Cl)_4$	–	−76	1.4590	1.5017	106.9	109.0

It is known that epichlorohydrin cannot be obtained from 2,3-dichloro-1-propanol by the action of alkalis; only 1,3-dichloro-2-propanol will give it under such conditions. Experiments in which the product of the reaction of Equation 3 was hydrolyzed and attempts were made to obtain epichlorohydrin from the dichloropropanol formed gave negative results, as against positive results obtained with pure 1,3-dichloro-2-propanol. Equations 1 and 2, therefore, represent the actual course of the process and the structures of the compounds obtained.

Epichlorohydrin and glycidol were treated not only with organochlorosilanes, but also with silicon tetrachloride. In the course of the work various methods for the preparation of epichlorohydrin and glycidol were examined and improved. It should be noted that the products of the reaction of organochlorosilanes with glycidol, alkyl(2-chloro-3-hydroxypropoxy)silanes, are unstable to hydrolysis and to heat, and we were unable to rectify many of them without decomposition; great difficulties were met in the analysis of these compounds.

TABLE 2

Substance	Formula	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	OH content (%)		Cl content (%)	
					found	calculated	found	calculated
(2-Chloro-3-hydroxypropoxy)-trimethylsilane.	$(CH_3)_3SiOCH_2CHClCH_2OH$	82-84 (18)	1.1331	1.4443	8.9	9.31	19.4	19.41
Bis(2-chloro-3-hydroxypropoxy)dimethylsilane.	$(CH_3)_2Si(OCH_2CHClCH_2OH)_2$	108 (20)	1.2267	1.4720	11.7	12.27	25.6	25.57
Tris(2-chloro-3-hydroxypropoxy)methylsilane.	$CH_3Si(OCH_2CHClCH_2OH)_3$	97 (16)	1.3219	1.4837	13.8	13.72	28.7	28.6

EXPERIMENTAL

1. Preparation of Epichlorohydrin

We obtained epichlorohydrin by the reaction of 1,3-dichloro-2-propanol with calcium hydroxide [6]. The 1,3-dichloro-2-propanol was prepared by saturating glycerol with hydrogen chloride [7]. It was found that the hydrolysis of silicon tetrachloride formed a very convenient method of preparing a continuous flow of hydrogen chloride for this purpose:

$$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl.$$

The hydrogen chloride was prepared in a reactor fitted with reflux condenser, thermometer, dropping funnel, and hermetically sealed stirrer. Water was introduced into the reactor and heated to 70-80°, and a mixture (1 : 1 by weight) of silicon tetrachloride and toluene was added gradually from the dropping funnel, the end of which was below the level of the water (toluene acted as a diluent). After passing through a drying system, the hydrogen chloride was passed to the vessel containing glycerol.

A 68% yield of 1,3-dichloro-2-propanol was obtained. It boiled at 72-76° (14 mm), its density was 1.359 ± 0.005, and its chlorine content was 53-55% (calculated 54.9%). The epichlorohydrin used in our experiments boiled at 115-118°. It had a chlorine content of 37.0-38.0% (calculated 37.8%) and an epoxy content of 44.0-46.6% (calculated 46.7%).

2. Preparation of Glycidol

Glycidol was prepared by the action of caustic soda on 3-chloro-1,2-propanediol [8]. It was obtained in 55-60% yield. It boiled at 61-63° (12 mm), and it had an epoxy content of 54% (calculated 58.01%). The characteristics of the organochlorosilanes and of the silicon tetrachloride used in the syntheses are given in Table 3.

TABLE 3

Silicon compound	Formula	B.p. (°C)	Chlorine content (%)
Trichloromethylsilane. . . .	CH_3SiCl_3	67	71.4
Dichlorodimethylsilane. . .	$(CH_3)_2SiCl_2$	69.5	55.1
Chlorotrimethylsilane. . . .	$(CH_3)_3SiCl$	57	32.7
Dichloromethylsilane. . . .	CH_3SiHCl_2	41	61.6
Trichloroethylsilane.	$C_2H_5SiCl_3$	97.5	65.4
Dichlorodiethylsilane. . . .	$(C_2H_5)_2SiCl_2$	129	45.2
Chlorotriethylsilane.	$(C_2H_5)_3SiCl$	143	23.4
Dichloroethylsilane.	$C_2H_5SiHCl_2$	74.5	54.8
Trichlorophenylsilane.	$C_6H_5SiCl_3$	201	50.3
Silicon tetrachloride.	$SiCl_4$	56	83.4

3. Reactions of Epichlorohydrin with Organochlorosilanes

Tris(2,3-dichloropropoxy)methylsilane. Epichlorohydrin (27.7 g, i.e. 0.3 mole) was placed in a flask fitted with reflux condenser, dropping funnel, thermometer, and hermetically sealed stirrer, and it was stirred while 14.9 g (0.1 mole) of trichloromethylsilane was added over a period of two hours. Reaction set in after the first few drops of trichloromethylsilane had been added, and the evolution of heat was only slight. The temperature in the flask was maintained within the range 27-35° by controlling the rate of addition of the trichloromethylsilane. When the addition was complete, the reaction mixture was stirred at the same temperature until tests for chloride (Volhard) and epoxy groups were negative (nine hours). The product, purified by exposure to a vacuum, was 38.3 g (89.9%) of tris(2,3-dichloropropoxy)methylsilane, n_D^{20} 1.4906; d_4^{20} 1.1452.

Found %: C 28.49; H 4.30; Si 6.22; Cl 49.18

$C_{10}H_{18}O_3SiCl_6$. Calculated %: C 28.11; H 4.21; Si 6.57; Cl 49.83

Bis(2,3-dichloropropoxy)dimethylsilane. This substance was prepared in a similar way from 28.8 g (0.3 mole) of epichlorohydrin and 19.3 g (0.15 mole) of dichlorodimethylsilane. The addition of dichlorodimethylsilane was spread over three hours; evolution of heat was observed immediately. The mixture was heated at 30-35° for ten hours. Vacuum fractionation then yielded 18.3 g (38.9%) of bis(2,3-dichloropropoxy)dimethylsilane, b.p. 160-165° (37 mm), n_D^{20} 1.4772; d_4^{20} 1.2720.

Found %: C 31.94; H 5.12; Si 8.20; Cl 44.07

$C_8H_{16}O_2SiCl_4$. Calculated %: C 30.58; H 5.09; Si 8.93; Cl 45.17

(2,3-Dichloropropoxy)trimethylsilane. This substance was prepared in a similar way from 31.4 g (0.33 mole) of epichlorohydrin and 36.1 g (0.33 mole) of chlorotrimethylsilane. Addition of the chlorotrimethylsilane was spread over three hours. The heating was at 30-35° for ten hours. Vacuum fractionation of the product yielded 10.2 g (15.3%) of (2,3-dichloropropoxy)trimethylsilane, b.p. 96-100° (66 mm), n_D^{20} 1.4456; d_4^{20} 1.1094.

Found %: C 35.83; H 7.16; Si 13.27; Cl 35.50
$C_6H_{14}OSiCl_2$. Calculated %: C 35.82; H 6.96; Si 13.76; Cl 35.27

Bis(2,3-dichloropropoxy)methylsilane. This substance was prepared in a similar way from 37.0 g (0.4 mole) of epichlorohydrin and 23.0 g (0.2 mole) of dichloromethylsilane. Addition of the dichloromethylsilane was spread over three hours; much heat was evolved. Heating was at 30-35° for ten hours. Vacuum fractionation of the product yielded 26.0 g (43.3%) of bis(2,3-dichloropropoxy)methylsilane, b.p. 173-175° (34 mm), n_D^{20} 1.4780; d_4^{20} 1.3740.

Found %: C 29.34; H 5.66; Si 8.95; Cl 47.23
$C_7H_{14}O_2SiCl_4$. Calculated %: C 28.01; H 4.66; Si 9.35; Cl 47.23

Tris(2,3-dichloropropoxy)ethylsilane. This substance was prepared in a similar way from 27.7 g (0.3 mole) of epichlorohydrin and 16.4 g (0.1 mole) of trichloroethylsilane. Addition of trichloroethylsilane was spread over 2 hours 30 minutes; heat was evolved. The further heating of the reaction mixture was at 38-40° for ten hours. The product was exposed to a vacuum to remove unchanged reactants, and 38.8 g (88.1%) of tris(2,3-dichloropropoxy)ethylsilane, n_D^{20} 1.4880; d_4^{20} 1.3740, was obtained.

Found %: C 30.31; H 5.00; Si 5.58; Cl 48.26
$C_{11}H_{20}O_3SiCl_6$. Calculated %: C 29.94; H 4.53; Si 6.36; Cl 48.25

Bis(2,3-dichloropropoxy)diethylsilane. This substance was prepared in a similar way from 27.7 g (0.3 mole) of epichlorohydrin and 23.5 g (0.15 mole) of dichlorodiethylsilane. Addition of dichlorodiethylsilane was spread over three hours; heat was evolved. The reaction mixture was then stirred at 40-50° for ten hours. Vacuum distillation yielded 5.2 g (10.1%) of bis(2,3-dichloropropoxy)diethylsilane, b.p. 150-200° (36 mm), n_D^{20} 1.4815.

Found %: C 34.21; H 6.09; Si 7.95; Cl 41.68
$C_{10}H_{21}O_2SiCl_4$. Calculated %: C 35.10; H 5.84; Si 8.21; Cl 41.47

(2,3-Dichloropropoxy)triethylsilane. This substance was prepared in a similar way from 18.5 g (0.2 mole) of epichlorohydrin and 30.1 g (0.2 mole) of chlorotriethylsilane. Addition of the chlorotriethylsilane was carried out at 40-50° and was spread over 90 minutes. The reaction mixture was then stirred at 40-50° for ten hours. Vacuum distillation yielded 15.8 g (32.6%) of (2,3-dichloropropoxy)triethylsilane, b.p. 65-70° (100 mm), n_D^{20} 1.4492; d_4^{20} 1.0776.

Found %: C 45.27; H 9.40; Si 11.60; Cl 30.22
$C_9H_{20}OSiCl_2$. Calculated %: C 44.53; H 8.22; Si 10.90; Cl 29.18

Bis(2,3-dichloropropoxy)ethylsilane. This substance was prepared in a similar way from 37.0 g (0.4 mole) of epichlorohydrin and 25.8 g (0.2 mole) of dichloroethylsilane. The reaction mixture was stirred at 30-35° for twelve hours. Vacuum distillation of the product yielded 46.7 g (74.5%) of bis(2,3-dichloropropoxy)ethylsilane, b.p. 185-190° (34 mm), n_D^{20} 1.4790; d_4^{20} 1.2992.

Found %: C 30.21; H 5.40; Si 8.83; Cl 45.17
$C_8H_{16}O_2SiCl_4$. Calculated %: C 30.58; H 5.09; Si 8.93; Cl 45.16

Tris(2,3-dichloropropoxy)phenylsilane. This substance was prepared in a similar way from 36.0 g (0.3 mole) of epichlorohydrin and 27.4 g (0.1 mole) of trichlorophenylsilane. Addition of the trichlorophenylsilane was spread over 90 minutes; heat was evolved. The reaction mixture was then stirred at 40-45° for 18 hours. The product was exposed to a vacuum to remove unchanged reactants, and 43.1 g (67.9%) of tri(2,3-dichloropropoxy)phenylsilane, n_D^{20} 1.5247; d_4^{20} 1.3666.

Found %: C 37.00; H 3.90; Si 5.96; Cl 44.74
$C_{15}H_{20}O_3SiCl_6$. Calculated %: C 36.82; H 3.70; Si 5.74; Cl 44.51

Tetrakis(2,3-dichloropropoxy)silane. This substance was prepared in a similar way from 37 g (0.4 mole) of epichlorohydrin and 17 g (0.1 mole) of silicon tetrachloride. Reaction was rather violent, and the silicon tetrachloride was added slowly, over a period of six hours, at 35-40°. The reaction mixture was then stirred at this temperature for twelve hours. The product was exposed to a vacuum to remove unchanged reactants, and 48.7 g (89.4%) of tetrakis(2,3-dichloropropoxy)silane, n_D^{20} 1.5017; d_4^{20} 1.4590, was obtained. It was not found possible to prepare this substance in an adequately pure form.

Found %: C 27.37; H 4.06; Si 5.14; Cl 51.94

$C_{12}H_{20}O_4SiCl_8$. Calculated %: C 26.68; H 3.71; Si 5.19; Cl 52.55

4. Reactions of Glycidol with Organochlorosilanes

(2-Chloro-3-hydroxypropoxy)trimethylsilane (2-Chloro-3-(trimethylsilyloxy)-1-propanol). Glycidol (16.2 g, i.e. 0.2 mole) was placed in a three-necked flask fitted with stirrer, thermometer, and dropping funnel, and protected with a calcium chloride tube. The glycidol was stirred, and 21.7 g (0.2 mole) of chlorotrimethylsilane was added with cooling to maintain the temperature at 25-28°. When the addition was complete the mixture was heated at 40-50° until test for chloride ions and epoxy groups were negative (two hours). Vacuum distillation of the product yielded 35 g (99%) of (2-chloro-3-hydroxypropoxy)trimethylsilane, b.p. 82-84° (18 mm), n_D^{20} 1.4443; d_4^{20} 1.1331. The purification and identification of products formed by reaction with glycidol were made difficult by the occurrence of a feeble side reaction between the chlorine atoms of the organochlorosilanes and the hydroxyl of glycidol.

Found %: C 40.4; H 8.5; Si 14.9; Cl 19.4; OH 8.9

$C_6H_{15}O_2SiCl$. Calculated %: C 39.43; H 8.28; Si 15.39; Cl 19.41; OH 9.31

Bis(2-Chloro-3-hydroxypropoxy)dimethylsilane (3,3'-(Dimethylsilylenedioxy)bis[2-chloro-1-propanol]). This substance was prepared in a similar way from 32.4 g (0.4 mole) of glycidol and 25.6 g (0.2 mole) of dichlorodimethylsilane. Yield 55 g (99%), b.p. 108° (20 mm), n_D^{20} 1.4720; d_4^{20} 1.2267.

Found %: C 34.8; H 6.6; Si 8.8; Cl 25.6; OH 11.7

$C_8H_{18}O_4SiCl_2$. Calculated %: C 34.64; H 6.54; Si 10.10; Cl 25.57; OH 12.27

Tris(2-chloro-3-hydroxypropoxy)methylsilane (3,3',3''-(Methylsilylidynetrioxy)tris[2-chloro-1-propanol]). This substance was prepared in a similar way from 24.3 g (0.3 mole) of glycidol and 15.0 g (0.1 mole) of trichloromethylsilane. Yield 27 g (75%), b.p. 97° (16 mm), n_D^{20} 1.4837; d_4^{20} 1.3219.

Found %: C 32.6; H 5.9; Si 6.9; Cl 28.7; OH 13.8

$C_{10}H_{21}O_6SiCl_3$. Calculated %: C 32.29; H 5.69; Si 7.54; Cl 28.62; OH 13.72

Bis(2-chloro-3-hydroxypropoxy)methylsilane (3,3'-(Methylsilylenedioxy)bis[2-chloro-1-propanol]). This substance was prepared in a similar way from 16.2 g (0.2 mole) of glycidol and 11.6 g (0.1 mole) of dichloromethylsilane. Yield 25 g (95%), n_D^{20} 1.4725. Owing to its high viscosity, this product—and also all those described below—were not distilled, but were exposed to a vacuum for two hours at 20° before being analyzed.

Found %: C 31.4; H 6.2; Si 9.3; Cl 26.5; OH 13.1

$C_7H_{16}O_4SiCl_2$. Calculated %: C 31.93; H 6.09; Si 10.64; Cl 26.99; OH 12.92

Bis(2-chloro-3-hydroxypropoxy)diethylsilane (3,3'-(Diethylsilylenedioxy)bis[2-chloro-1-propanol]). This substance was prepared in a similar way from 16.2 g (0.2 mole) of glycidol and 15.6 g (0.1 mole) of dichlorodiethylsilane. Yield 30 g (98%), n_D^{20} 1.4770; d_4^{20} 1.2063.

Found %: C 40.0; H 7.9; Si 8.9; Cl 22.7; OH 12.0

$C_{10}H_{22}O_4SiCl_2$. Calculated %: C 39.33; H 7.26; Si 9.17; Cl 23.24; OH 11.14

Tris(2-chloro-3-hydroxypropoxy)ethylsilane (3,3',3''-(Ethylsilylidynetrioxy)tris[2-chloro-1-propanol]). This substance was prepared in a similar way from 24.3 g (0.3 mole) of glycidol and 16.3 g (0.1 mole) of trichloroethylsilane. Yield 24 g (62%), n_D^{20} 1.4880; d_4^{20} 1.3142.

Found %: C 34.1; H 6.6; Si 7.5; Cl 26.6; OH 12.4

$C_{11}H_{23}O_6SiCl_3$. Calculated %: C 34.24; H 6.02; Si 7.26; Cl 27.58; OH 13.22

Bis(2-chloro-3-hydroxypropoxy)ethylsilane (3,3'-Ethylsilylenedioxy)bis[2-chloro-1-propanol]). This substance was prepared in a similar way from 16.2 g (0.2 mole) of glycidol and 12.9 g (0.1 mole) of dichloroethylsilane. Yield 25 g (93%); n_D^{20} 1.4810.

Found %: C 34.8; H 6.5; Si 9.8; Cl 24.8; OH 12.5

$C_8H_{18}O_4SiCl_2$. Calculated %: C 34.65; H 6.54; Si 10.10; Cl 25.59; OH 12.27

Tris(2-chloro-3-hydroxypropoxy)phenylsilane (3,3',3''-Phenylsilylidynetrioxy)tris[2-chloro-1-propanol]). This substance was prepared similarly from 16.2 g (0.2 mole) of glycidol and 13.9 g (0.066 mole) of trichlorophenylsilane. Yield 24 g (85%), n_D^{20} 1.5210; and d_4^{20} 1.3256.

Found %: C 40.0; H 6.0; Si 5.9; Cl 24.4; OH 12.5

$C_{15}H_{23}O_6SiCl_3$. Calculated %: C 41.51; H 5.34; Si 6.45; Cl 23.34; OH 12.57

Tetrakis(2-chloro-3-hydroxypropoxy)silane. This substance was prepared similarly from 16.2 g (0.2 mole) of glycidol and 8.5 g (0.05 mole) of silicon tetrachloride. Yield 15 g (67%) n_D^{20} 1.4925.

Found %: C 30.8; H 5.6; Si 5.5; Cl 29.2; OH 15.7

$C_{12}H_{24}O_8SiCl_4$. Calculated %: C 30.89; H 5.19; Si 6.01; Cl 30.42; OH 14.56

5. Hydrolysis of (2,3-Dichloropropoxy)trimethylsilane and Identification of the Dichloropropanol Formed

a) A mixture of 44 g (0.22 mole) of (2,3-dichloropropoxy)trimethylsilane, 18 g (1 mole) of distilled water, and 1.45 g of hydrochloric acid, sp.gr. 1.17 was prepared in a conical flask fitted with a thermometer and was then shaken continuously for 90 minutes. During the shaking the temperature of the reaction mixture rose to 30-35°, and separation into three layers was observed. After the hydrolysis the reaction mixture was separated in a separating funnel. Distillation of the upper layer yielded 14.5 g (81%) of hexamethyldisiloxane, b.p. 101°. Vacuum distillation of the lower layer yielded 19.5 g (68%) of a dichloropropanol, b.p. 87-88° (5 mm).

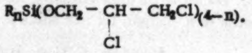
b) Dichloropropanol obtained by the hydrolysis of (2,3-dichloropropoxy)trimethylsilane (16 g, i.e. 0.124 mole) was placed in a Claisen flask, and 13 g of distilled water was added.

Freshly calcined calcium oxide (7.8 g) was weighed into a porcelain dish and slaked with 5 g of water. The slaked lime was transferred to the Claisen flask, which was then shaken vigorously until separation of layers occurred (90 minutes). The liquid that separated was distilled, and the distillate, which came over at 62-70° (60 mm), separated into two layers. The lower layer was separated in a separating funnel and distilled at atmospheric pressure. No epichlorohydrin was obtained.

A control experiment was carried out in a similar way with 1, 3-dichloro-2-propanol, and 4.9 g (39.5%) of epichlorohydrin (b.p. 115-118°; epoxy content 43.3%) was obtained.

SUMMARY

1. The reaction of epichlorohydrin with organochlorosilanes leads to the formation of alkyl (2,3-dichloropropoxy)silanes. Ten new compounds of general formula



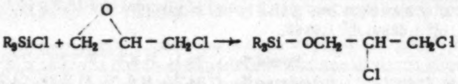
$$R_nSi(OCH_2-\underset{\displaystyle Cl}{CH}-CH_2Cl)_{(4-n)}.$$

($R = CH_3, C_2H_5, C_6H_5$) were synthesized, and their properties were studied.

2. Glycidol reacts with organochlorosilanes with participation of the epoxide ring, which is opened. Under the conditions described, the hydroxyl group either does not react, or reacts only to a slight extent. Nine new compounds were synthesized from glycidol and organochlorosilanes, their general formula being

$$R_nSi(OCH_2CHCl-CH_2OH)_{(4-n)}.$$

3. It was established that in the reaction of unsymmetrical α-epoxides with organochlorosilanes opening of the epoxide ring proceeds according to the scheme:



$$R_3SiCl + \overset{\displaystyle O}{CH_2-CH}-CH_2Cl \rightarrow R_3Si-OCH_2-\underset{\displaystyle Cl}{CH}-CH_2Cl$$

LITERATURE CITED

[1] R. Sauer, W. Patnode, J. Am. Chem. Soc. 67, 1548 (1945).

[2] W. Gilliam, R. Meals, R. Sauer, J. Am. Chem. Soc. 68, 1161 (1946).

[3] German Pat. 802895, 803079, and others.

[4] U. S. Pat. 2389802.

[5] K. Michael, Ber. 39, 2789 (1906).

[6] Organic Syntheses, Collected Vol. 2, Foreign Lit. Press, Moscow, 1949, p. 573.

[7] Organic Syntheses, Collected Vol. 1, Foreign Lit. Press, Moscow, 1949, p. 213.

[8] I. Houben, Methods of Organic Chemistry, Vol. 3, Part 1, United Sci. Tech. Press, Moscow and Leningrad, (Trans) 1934, p. 252.

Received May 13, 1954

V. I. Lenin Electrotechnics Institute

BLANK PAGE

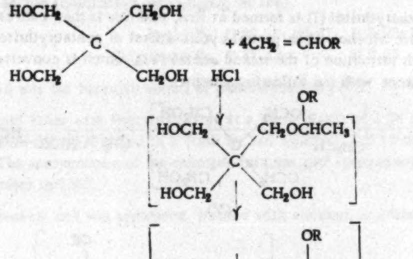
REACTIONS BETWEEN VINYL COMPOUNDS AND MULTIFUNCTIONAL COMPOUNDS

COMMUNICATION 6. REACTION OF VINYL ETHERS WITH PENTAERYTHRITOL

M. F. Shostakovsky, A. S. Atavin, and V. V. Zhebrovsky

We have shown previously that vinyl ethers react with glycols [1, 2], glycerol [3, 4], and polyvinyl alcohol [5] with formation of cyclic acetals. By the reaction of glycerol with vinyl ethers under various conditions we have prepared partial cyclic acetals, diglycerol triacetal, and mixed cyclic acetals containing an O-(1-alkoxyethyl) group. It was of interest in this connection to investigate the reactions of vinyl ethers with polyhydric alcohols containing even numbers of hydroxyls, such as pentaerythritol, the conditions being then favorable for the formation of full cyclic acetals.

In the reaction of vinyl ethers with pentaerythritol, it might be expected that the process would at first take the following directions:



(I)

(II)

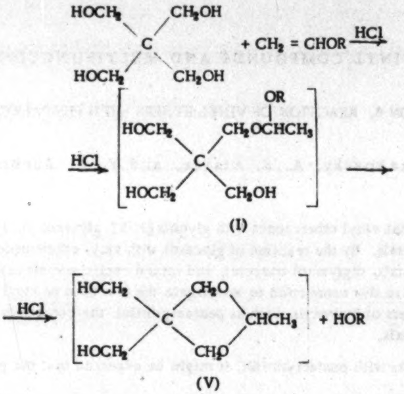
(III)

(IV)

(R = C_2H_5, C_4H_9).

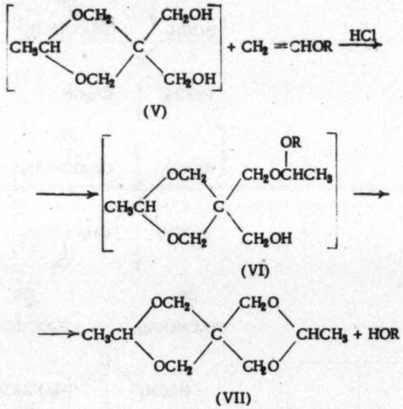
This should lead to the formation of mixed acetals of pentaerythritol with monohydric alcohols in a series of increasing degree of substitution, (I), (II), (III), and (IV). In the present investigation, however, none of these acetals was isolated.

On the basis of our previous investigations and of the experimental results of the present investigation, it is more probable that reaction of alkyl vinyl ethers with pentaerythritol, which leads finally to the formation of the bicyclic acetal of pentaerythritol, proceeds according to the following scheme:



(R = C_2H_5, C_4H_9)

The partial acetal of pentaerythritol (I) is formed at first, and this is then converted into the cyclic acetal (V) with elimination of monohydric alcohol. The partial cyclic acetal of pentaerythritol then reacts with another molecule of alkyl vinyl ether with formation of the mixed acetal (VI), which is converted into the bicyclic acetal of pentaerythritol (VII) in accordance with the following scheme:



In the course of the investigation we have isolated the bicyclic acetal of pentaerythritol (VII), the acetaldehyde dialkyl acetals, and the alcohols themselves. It is clear that the formation of the dialkyl acetals in the synthesis of the bicyclic acetal of pentaerythritol (VII) results mainly from the reaction of the vinyl ethers with alcohols eliminated in the cyclization reactions. The present investigation shows that the bicyclic acetal (VII) is formed with various proportions of reactants, including those in which the vinyl ether is in excess. The pentaerythritol acetal (VII) was prepared by Nieuwland [6] by the action of acetylene on pentaerythritol in presence of mercuric oxide and boron trifluoride.

It may probably be assumed that in the formation of the bicyclic acetal of pentaerythritol (VII) cyclization of the mixed acetal (I) and later of the acetal (VI) proceeds more rapidly than the addition of alkyl vinyl ether to all four hydroxyls of the pentaerythritol. As already pointed out, in the synthesis of the bicyclic acetal (VII) a monohydric alcohol is elminated, and this reacts with free alkyl vinyl ether with formation of the corresponding acetal.

Thus, part of the vinyl ether is consumed in the formation of the dialkyl acetal, and it was found that the highest yield of the bicyclic acetal of pentaerythritol (VII) was obtained when excess of the alkyl vinyl ether was used.

EXPERIMENTAL

For the synthesis of the acetals the following substances were used: ethyl vinyl ether, b.p. 35.9°, d_4^{20} 0.7533; n_D^{20} 1.3778; butyl vinyl ether, b.p. 93.7-93.8°, d_4^{20} 0.7791; n_D^{20} 1.4029; and pentaerythritol, m.p. 253°.

a) Reaction of Ethyl Vinyl Ether with Pentaerythritol at a Molar Ratio of 7.1 : 1. A mixture of 20 g of pentaerythritol and 75.3 g of ethyl vinyl ether was prepared in a flask fitted with mercury-sealed stirrer, reflux condenser, and thermometer, and six drops of hydrochloric acid (0.084 g of HCl) were added; the temperature of the reaction mixture rose to 78°. The reaction product, which was dark in color, was neutralized with potassium carbonate and fractionated from a Favorsky flask under reduced pressure, when the following fractions were obtained:

Frac. I	b.p. to 33° (35 mm);	4.5 g
Frac. II	b.p. to 28° (22 mm);	9 g
Frac. III	b.p. 106-110° (9 mm);	13 g (solidified)
Residue		65 g (resinous mass)

Fraction I was ethyl alcohol containing some acetaldehyde diethyl acetal. After being redistilled Fraction II boiled at 20° (22 mm) and had n_D^{20} 1.3820, which corresponds to acetaldehyde diethyl acetal (the literature [7] gives n_D^{20} 1.3820). After being recrystallized from alcohol Fraction III melted at 40°; its molecular weight, determined cryoscopically in benzene, was M 186 (calculated for $C_9H_{16}O_4$, M 188).

Found %:	C 57.76; 57.67;	H 8.23; 8.50
Calculated %:	C 57.42;	H 8.56

The substance so isolated was the bicyclic acetal of pentaerythritol (VII).

b) Reaction of Butyl Vinyl Ether with Pentaerythritol at a Molar Ratio of 2.24 : 1. Pentaerythritol (20 g) and butyl vinyl ether (32.8 g) were stirred together in a flask for ten minutes, and 15 drops of hydrochloric acid (0.210 g of HCl) were added. The temperature of the reaction mixture rose spontaneously to 72°, when the liquid boiled; the temperature rose further to 128°.

Some precipitate was present, and was separated, washed with acetone, and dried. It was found to be pentaerythritol.

After being neutralized with potassium carbonate, the liquid was fractionated, the following fractions being obtained:

Frac. I,	b.p. 117-122°	11 g; n_D^{20} 1.3997
Frac. II,	b.p. 58-65° (for 7 mm);	10 g; n_D^{20} 1.4096
Frac. III,	b.p. 98-106° (for 7 mm);	13 g;
	Residue	10 g

After being redistilled Fraction I boiled at 117-118.5° and had n_D^{20} 1.3990 and d_4^{20} 0.8105. These constants correspond to butyl alcohol, for which the literature [8] gives b.p. 117-118° and n_D^{20} 1.3983. The yield of butyl alcohol was 9.6 g.

Fraction II was redistilled and then had b.p. 60-61° (7 mm), n_D^{20} 1.4090, and d_4^{20} 0.8269. These constants correspond to acetaldehyde dibutyl acetal, for which the literature [9] gives n_D^{20} 1.4090 and d_4^{20} 0.8267. The yield was 8 g.

Fraction III solidified when allowed to stand. After being recrystallized from alcohol it melted at 40°. Found M 186 (cryscopically in benzene); for $C_9H_{16}O_4$ calculated M 188. The substance so isolated was the bicyclic acetal of pentaerythritol (VII).

c) Reaction of Butyl Vinyl Ether with Pentaerythritol at a Molar Ratio of 5.2 : 1. Pentaerythritol (20 g) and butyl vinyl ether (76.4 ml) were stirred together in a flask for 30 minutes, and 15 drops of hydrochloric acid (0.21 g of HCl) were added; the temperature rose to 130°. The reaction mixture was an oily mass that darkened in the air. It was neutralized with potassium carbonate and distilled, when the following fractions were obtained:

Frac. I,	b.p. 116-125°;	12 g
Frac. II,	b.p. 58-62 (for 7 mm);	20 g
Frac. III,	b.p. 98-110° (for 7 mm);	29 g
	Residue 33 g	

Redistillation of Fraction I yielded 10 g of a substance boiling at 117-118° and having n_D^{20} 1.3992, corresponding to butyl alcohol.

After being refractionated Fraction II had b.p. 60-61° (7 mm), n_D^{20} 1.4099, and d_4^{20} 0.8269, corresponding to acetaldehyde dibutyl acetal.

Crystallization of Fraction III from alcohol yielded 21 g of a crystalline substance, m.p. 40°. Found M 187; Found M 187; for $C_9H_{16}O_4$ calculated M 186. The substance so isolated was the bicyclic acetal of pentaerythritol (VII).

SUMMARY

1. The reactions of alkyl vinyl ethers (the ethyl and butyl ethers) with pentaerythritol were studied for various proportions of the reactants.

2. It was shown that an alkyl vinyl ether reacts with pentaerythritol in presence of hydrochloric acid with formation of the bicyclic acetal of pentaerythritol, the dialkyl acetal of acetaldehyde, and the monohydric alcohol.

LITERATURE CITED

[1] M. F. Shostakovsky, N. A. Gershtein, et al., Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, No 4, 671.*

[2] M. F. Shostakovsky, V. V. Zhebrovsky, and M. A. Medelyanovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No.4, 683.**

[3] M. F. Shostakovsky, V. V. Zhebrovsky, and M. A. Medelyanovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No.1, 166.***

[4] M. F. Shostakovsky, V. V. Zhebrovsky, and M. A. Medelyanovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No.2, 354.****

[5] M. F. Shostakovsk V. V. Zhebrovsky, and M. A. Medelyanovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No.3, 535. *****

[6] J. A. Nieuwland, R. R. Vogt, H. Foohey, J. Am. Chem. Soc. 1018, (1930).

[7] M. F. Shostakovsky, Vinyl Ethers, Acad. Sci. USSR Press, 1952, p. 203.

[8] Short Handbook of Chemistry, 1951, p. 166.

[9] M. F. Shostakovsky and N. A. Gershtein, J. Gen. Chem. 16, 6, 937(1946).

Received January 27, 1954

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

---

* Consultant's Bureau Translation, p 617.

** Consultant's Bureau Translation, p 583.

*** Consultant's Bureau Translation, p 137.

**** Consultant's Bureau Translation, p 317.

***** Consultant's Bureau Translation, p 455.

OPTICAL INVESTIGATION OF SOME VINYL ETHERS OF ETHANOLAMINES

M. F. Shostakovsky, M. I. Batuev, I. A. Chekulaeva, and A. D. Matveeva

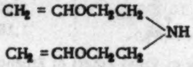
Chemical and optical investigations of monovinyl ethers of glycols and polyethylene glycols have shown that the chemical inertness of these substances in several reactions that are characteristic of vinyl ethers [1] is to be explained by the formation of intermolecular hydrogen bonds, which "block" the hydrogen of the hydroxyl group [2]. As is well known, hydrogen bonds of the types N − H....O, O − H....N, and N − H...N occur in compounds of various kinds (amines, amides, etc.), and their presence has been confirmed optically, like that of the hydrogen bond of the type O − H...O in aliphatic alcohols, aliphatic acids, monovinyl ethers of glycols and polyethylene glycols, etc. The observed chemical inertness of vinyl ethers of ethanolamines ($CH_2 = CHOCH_2-CH_2NH_2, CH_2 = CHOCH_2CH_2NHR$) has led us to assume that hydrogen bonds of the types N − H...O and N − H-...N are formed in these compounds.

The fact that it has not been found possible to bring about the addition of alcohols to vinyl ethers of ethanolamines and to effect their cyclization and polymerization in presence of ionic catalysts is to be explained by the presence of a hydrogen bond, associated with the ability of nitrogen to give onium compounds. On the other hand, vinyl ethers of ethanolamines whose structures preclude the formation of hydrogen bonds ($CH_2 = CHOCH_2CH_2NR_2$) do not show this chemical inertness [3]. These considerations prompted us to make a special investigation of some vinyl ethers of ethanolamines with the object of determining what hydrogen bonds were present.

We investigated:

The vinyl ether of 2-aminoethanol $CH_2 = CHOCH_2CH_2NH_2$ (I)

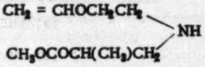
The divinyl ether of diethanolamine



$$(CH_2 = CHOCH_2CH_2)_2NH$$

(II)

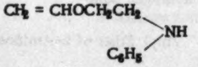
The methyl ester of 2-methyl-3-[(2-vinyloxyethyl)amino]propionic acid



$$CH_2 = CHOCH_2CH_2-NH-CH_2CH(CH_3)COOCH_3$$

(III)

The vinyl ether of 2-anilinoethanol



$$CH_2 = CHOCH_2CH_2-NH-C_6H_5$$

(IV)

Monoethanolamine (2-aminoethanol) (taken for optical comparison) $HOCH_2CH_2NH_2$ (V)

The vinyl ether (I), (II), and (IV) were prepared by the vinylation of the corresponding amino alcohols [3, 4], and the vinyl ether (III) was prepared by reaction of the vinyl ether of 2-aminoethanol with methyl methacrylate [5]. The constants of these compounds are given in Table 1.

It was natural to turn first to the cryoscopic determination of the degree of association of the vinyl ethers of ethanolamines. We carried out this determination for three of the ethers in benzene solution; 2-aminoethanol is insoluble in benzene. The results of the determination are given in Table 2. They show that, even in solutions of fairly high concentration, the degree of association of these ethers is close to unity.

We may infer from this that vinyl ethers of ethanolamines do not tend to form long associated chains or cyclic dimer complexes (schemes (a) and (b)) to any appreciable extent. If a hydrogen bond is formed in these compounds, then it can only be an intramolecular bond (scheme (c)). The cryoscopic results, however, cannot in themselves answer the question of whether such an intramolecular hydrogen bond exists in these ethers, or whether it is in general absent. Suitable optical investigations (by Raman spectra) can answer this question.

In the liquid phase compounds containing amino (NH_2) and imino (NH) groups are generally associated by means of hydrogen bonds (N − H...N, or N − H...O, if the compound also contains oxygen). The participation of N − H in a hydrogen bond is manifested optically by a lowering of the vibrational frequency of the N − H bond. Lines corresponding to these frequencies are not smeared out into wide continuous bands (as for methyl and ethyl alcohols and for monovinyl ethers of glycols and polyethylene glycols, but are only broadened somewhat. The most intense of these form broad lines, sometimes almost narrow bands •.

TABLE 1

Physical Constants of Vinyl Ethers of Ethanolamines, and also of 2-Aminoethanol

Compound	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}
Vinyl ether of 2-aminoethanol. . . .	115-116 (735)	1.4390	0.9018
Divinyl ether of diethanolamine. . .	68-69 (3.5)	1.4576	0.9491
Methyl ester of 2-methyl-3-[(2-vinyloxyethyl)amino]propionic acid.	97.5 (4)	1.4491	0.9998
Vinyl ether of 2-anilinoethanol. . . .	108-109 (3.5)	1.5523	1.0295
2-Aminoethanol.	169-170	1.4555	1.013

TABLE 2

Cryoscopic Determination of the Degree of Association of Vinyl Ethers of Ethanolamines in Benzene Solution

Vinyl ether of 2-aminoethanol		Divinyl ether of diethanolamine		Vinyl ether of 2-anilinoethanol	
Concentration (mole-%)	Degree of association	Concentration (mole-%)	Degree of association	Concentration (mole-%)	Degree of association
0.865	1.015	0.4075	1.000	2.216	0.9934
1.275	1.109	1.5475	1.000	4.277	1.037
3.724	1.140	3.1150	1.000	6.988	1.073
5.457	1.169	6.2710	1.036	9.739	1.085
13.450	1.306	8.0940	1.054	16.16	1.178
20.92	1.396	16.970	1.073	–	–
–	–	24.95	1.161		–

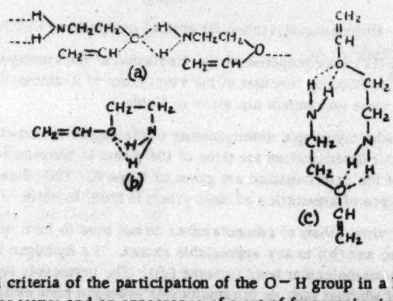
Possible Kinds of Hydrogen Bonds in Vinyl Ethers of Ethanolamines

(a) Association into long chains

(b) Association into a cyclic dimer

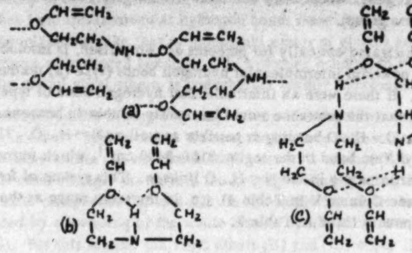
(c) Intramolecular hydrogen bond

Vinyl Ether of 2-Aminoethanol (I)

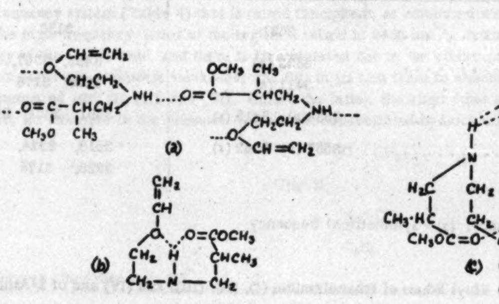


• The main optical criteria of the participation of the O−H group in a hydrogen bond are a displacement in the direction of the longer waves and an appearance of a set of frequencies in the region that is characteristic for the hydroxyl group. The smearing out of these frequencies in the liquid phase into a wide continuous band is due to various disturbances in short-range order in the liquid (quasi-crystalline) state of matter, and not to the formation of a hydrogen bond, as such; it is a secondary effect of hydrogen bonding found in the liquid phase [6]. When NH_2 or NH groups participate in hydrogen bonding, this secondary effect is found only rarely.

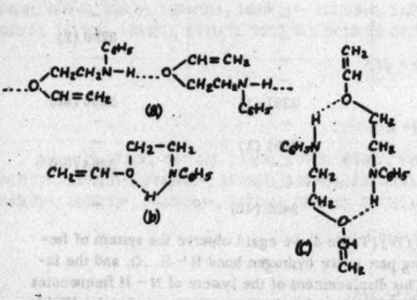
Divinyl Ether of Diethanolamine (II)



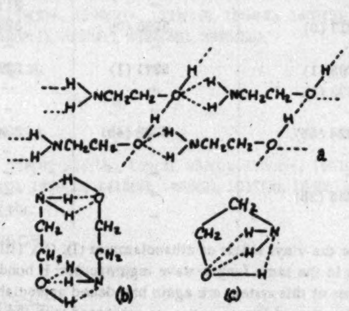
Methyl Ester of 2-Methyl-3-[(2-vinyloxyethyl)amino]propionic Acid (III)



Vinyl Ether of 2-Anilinoethanol (IV)



2-Aminoethanol (V)



In Table 3, by way of example, we show the lowering of the vibrational frequencies of the N – H bond for several compounds as we pass from the gas phase (isolated molecules) to the liquid phase (molecules associated by means of the hydrogen bond N – H...O or N – H...N). Table 3 shows that the frequency of the N – H bond in isolated molecules lies in a fairly high region – about 3500 cm^{-1} and even higher (vibrations of the imino group and asymmetrical vibrations of the amino group).

2-Aminoethanol, which we investigated optically for purposes of comparison, is insoluble in benzene. This fact is an indication that forms very powerful intermolecular hydrogen bonds (type (a) reather than type (b)) which are not broken down by benzene. If there were an intermolecular hydrogen bond of type (c), or even a cyclic dimer of type (b), it would be expected that the substance would be readily soluble in benzene. In 2-aminoethanol, but not in vinyl esters of ethanolamines, O – H...O bonding is possible as well as N – H...O. The O – H...O linkage is evidenced by a characteristic highly diffuse band in the region 3150-3400 cm^{-1}, which forms a background to the system of bands of the NH_2 group participating in the N – H...O linkage. This system of frequencies is distributed over the range 8145-3364 cm^{-1} (see Column V in Table 4), i.e. in the same range as that of the frequencies of the associated molecules of the compounds listed in Table 3.

TABLE 3

Vibrational Frequencies of the N – H Bond of Certain Compounds in the Gas and Liquid Phases [7]

Compound	Vibrational frequencies (cm^{-1})	
	Gas phase	Liquid phase
HNCO	3531	3133
$HCONH_2$	3533 (a) 3411 (s)	3499, 3307, 3228, 3176
CH_3CONH_2	3533(a), 3415 (s)	3501, 3351, 3190
$C_2H_5OOCNH_2$	3557 (a) 3442 (s)	3513, 3324, 3226, 3176

(a) - asymmetrical frequency; (s) - symmetrical frequency

TABLE 4

Frequencies of the N – H Bonds of the Vinyl Ethers of Ethanolamines (I), (II), (III), and (IV) and of 2-Aminoethanol (the vinyl ethers (I), (II), (III), and (IV) are given in the same order as before)

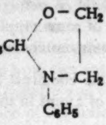
I	II	III	IV	V
–	–	–	–	3145 (1)
–	–	3176 (1)	–	3187 (3)
3217 (0)	3225 (0)	3224 (1)	–	–
–	–	–	–	3239 (2)
3263 (1)	3271 (1)	3274 (1)	–	–
3293 (1)	–	–	–	–
–	–	–	3301 (1)	3300 (6b)
3324 (5b)	3338 (4b)	3343 (4b)	–	–
–	–	–	3351 (1)	–
–	–	–	–	3364 (3b)
3385 (3b)	–	–	–	–
–	–	–	3406 (4b)	–

For the vinyl ethers of ethanolamines (I), (II), (III), and (IV) (Table 4) we again observe the system of frequencies in the same longer-wave region for N – H bonds taking part in the hydrogen bond N – H...O, and the intense lines of this system are again broadened appreciably. This displacement of the system of N – H frequencies in the direction of longer waves, as compared with the frequencies of these bonds in monomeric molecules (Tables 3 and 4) is an indisputable proof of the presence of hydrogen bonds in these compounds. Taking into account the cryoscopic data given above, we must conclude that in these compounds ((I), (II), (III), (IV)) intramolecular hydrogen bonding is overwhelmingly predominant ((Ic), (IIc), (IIIc), and (IVc)). It should be noted that a certain simplification of the system of N – H frequencies in (II), (III), and (IV), as compared with (I) and (V) (fewer intensive lines – one, instead of two or three), is to be attributed to the replacement of a hydrogen atom of the amino group by a radical.

Hence, the higher reactivity that we have observed in those vinyl ethers of ethanolamines whose structures clearly exclude the possibility of hydrogen bonding together with the results of the optical investigation of four chemically inert ethers that form intramolecular hydrogen bonds show that the chemical inertness of the investigated vinyl ethers of ethanolamines, like that of monovinyl ethers of glycols and polyethylene glycols [2], is associated with the occurrence of hydrogen bonding. The hydrogen bonding in vinyl ethers of ethanolamines, however, unlike that in the glycol vinyl ethers, is undoubtedly mainly intramolecular, not intermolecular.

By varying the substituent on the nitrogen in vinyl ethers of ethanolamines, we may alter the strength of the intramolecular hydrogen bond – and therefore the reactivity – and follow this alteration optically. Thus, in the divinyl ether of diethanolamine (II) and the methyl ester of 2-methyl-3-[(2-vinyloxyethyl)amino]propionic acid (III) the $>$NH group is more strongly drawn into the hydrogen bond as a result of the participation of the two oxygen atoms present in these compounds (IIc and IIIc) in the formation of the bond. The strengthening of the hydrogen bond is manifested by a lowering of the whole system of N – H frequencies in (II) and (III), as compared with (I) and (IV) (Table 4). For this reason, the vinyl ethers (II) and (III) differ little in their chemical inertness in reactions characteristic for vinyl ethers from the vinyl ether of 2-aminoethanol (I); they are extremely inert chemically.

However, when one hydrogen of the vinyl ether (I) is replaced by phenyl, notable changes in the chemical and optical behavior of the compound are to be observed. Thus, in contrast with (II) and (III), the compound (IV) has an N – H frequency system (Table 4) that is raised throughout, as compared with the system of (I) and (V); in particular, the high-frequency limit of the region is raised to 3406 cm^{-1}. Introduction of the phenyl radical raises the energy of the N – H bond, and there is an associated rise in the vibrational frequency. As a result NH...O hydrogen bonds are somewhat weakened, and this in its turn leads to enhanced reactivity in the vinyl ether (IV), as compared with (I), (II), and (III). Unlike the latter, the vinyl ether of 2-anilinoethanol (IV) is readily cyclized, for example in the presence of traces of concentrated hydrochloric acid, with formation of

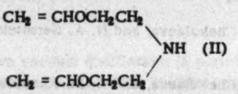


and it also undergoes other reactions [3].

We give below the complete Raman spectra of the investigated compounds (I), (II), (III), (IV), and (V). The spectra were measured with a Soviet spectrograph ISP-51 with the medium camera.

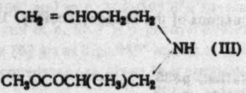
$$CH_2 = CHOCH_2CH_2NH_2 \quad (I)$$

$\Delta\nu$ cm^{-1}: 169(2), 248 (4b), 285(0), 324(2)*, 352(2)*, 404(1), 435(1), 498(4), 603(3), 644(0), 710(2), 821(5b), 904(4), 966(4), 996(4), 1084(2)*, 1099(3)*, 1113(3)*, 1157(1), 1179(2)*, 1209(2)*, 1321(10), 1354(2), 1407(2), 1461(5), 1617(8), 1637(7), 2871(7), 2932(8b), 3018(3), 3217(0), 3263(1), 3293(1), 3324(5b), 3385(3b).



$$(CH_2 = CHOCH_2CH_2)_2NH \quad (II)$$

$\Delta\nu$ cm^{-1}: 171(2), 241(4b), 503(3), 609(3), 660(0), 745 (0);, 778(0), 826(5b), 892(3), 935(0), 972(3)*, 1001(2)*, 1032(3)*, 1067(2)*, 1102(2)*, 1149(3)*, 1203(3), 1263(3), 1322(10), 1364(0), 1389(1), 1413(2), 1463(3), 1617(8), 1642(7), 2842(2)*, 2876(7)*, 2938(8b)*, 3022(4), 3225(0), 3271(1), 3338(4b).



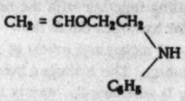
$$CH_2 = CHOCH_2CH_2NHCH_2CH(CH_3)COOCH_3 \quad (III)$$

$\Delta\nu$ cm^{-1}: 163(1), 188(1), 236(3b), 324(1), 366(1), 431(0), 468(0), 505(1b), 611(0b), 658(0b), 708(1), 768(1),

---

* On a background.

813(1), 838(6b), 903(2b), 935(0), 973(3), 991(3), 1029(0), 1056(0), 1104(1), 1152(1b), 1206(1b), 1321(10), 1366(1), 1419(1), 1463(8), 1619(6), 1637(5), 1660(2), 1698(1), 1737(4), 2880(6)*, 2943(10b)*, 2972(3)*, 3020(2), 3082(0), 3176(1), 3224(1), 3274(1), 3343(4b).



$CH_2=CHOCH_2CH_2NH(C_6H_5)$ (IV)

$\Delta \nu$ cm^{-1}: 125(2), 178(1), 214(2)*, 233(2)*, 248(2)*, 414(4b), 490(1)*, 510(1)*, 531(1)*, 576(0)*, 596(1)*, 619(4)*, 646(0), 663(0), 752(4), 782(4), 815(5), 833(0), 852(5), 871(0), 916(1), 993(10), 1029(5), 1073(0), 1155(4), 1182(3), 1199(0), 1287(1), 1320(5), 1356(0), 1380(0), 1408(0), 1434(0), 1455(1), 1493(1), 1603(10), 1619(1)*, 1639(1)*, 2850(0), 2876(4), 2933(4), 2984(0), 3024(1), 3301(1), 3351(1), 3406(4b).

$HOCH_2CH_2NH_2$ (V)

$\Delta \nu$cm^{-1}: 171(1), 482(4), 522(2), 838(4), 874(5), 1034(3), 1065(4), 1083(5), 1108(4), 1173(2b), 1248(3b), 1298(5), 1313(5), 1359(4b), 1460(10), 1593(1b)*, 2707(3b)**, 2862(10)**, 2914(9)**, 2942(9)**, 3145(1)***, 3187(3)***, 3239(2)***, 3300(6b)***. 3364(3b)***. 3150-3400 (OH band).

---

* Composite frequency: 482 + 1108 = 1590 (and others).

** On a background

*** On a background of the OH band.

SUMMARY

1. The Raman spectra were determined for the vinyl ethers of 2-aminoethanol and of 2-anilinoethanol, the divinyl ether of diethanolamine, the methyl ester of 2-methyl-3-[(2-vinyloxyethyl)amino]propionic acid, and 2-aminoethanol.

2. It was proved that intramolecular hydrogen bonding occurs in these compounds.

3. It was shown that the chemical inertness of some vinyl ethers of ethanolamines in ionic reactions is associated with the presence of hydrogen bonds in their molecules.

4. A study was made of the dependence of the chemical inertness of vinyl ethers of ethanolamines on their chemical structure, i.e. on the mutual effects of atoms in the molecule.

LITERATURE CITED

[1] M. F. Shostakovsky, Vinyl Ethers, Acad. Sci. USSR Press, Moscow, 1952.

[2] M. F. Shostakovsky, M. I. Batuev, P. V. Tyupaev, and A. D. Matveeva, Proc. Acad. Sci. USSR 89, 93 (1953); 89, 501 (1953); Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No. 6, 1103.

[3] M. F. Shostakovsky and I. A. Chekulaeva, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, No 2, 368;* 1954, No.6, 1111; 1955, No 1, 146 **.

[4] M. F. Shostakovsky, I. A. Chekulaeva, and N. A. Gershtein, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1951, No 3, 328.

[5] M. F. Shostakovsky, I. A. Chekulaeva, and A. M. Khomutov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No 2, 323. ***

[6] M. I. Batuev, J. Phys. Chem. 23, 1399 (1949); 25, 884(1951); Bull. Acad. Sci. USSR, Physical Series 14, 429 (1950).

[7] G. Herzberg, C. Reid, Discussions of the Faraday Society, 1950, No 9, p. 92; M. Davies, J. Evans, J. Chem. Phys. 20, 342 (1952).

---

* Consultant's Bureau Translation, p335.

** Consultant's Bureau Translation, p 127.

*** Consultant's Bureau Translation, p 263.

Received January 27, 1954

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

MACROMOLECULAR COMPOUNDS

COMMUNICATION 74. EFFECT OF AROMATIC COMPONENTS ON THE PROPERTIES OF MIXED POLYAMIDES

V. V. Korshak and T. M. Frunze

We have previously described the results of investigations on binary polyamide systems derived from mixtures of various proportions of two 1,6-hexanediamine salts of dicarboxylic acids [1], and also on binary systems derived from a mixture of 6-caprolactam (2-oxohexamethylenimine) and a 1,6-hexanediamine salt of a dicarboxylic acid [2]; various dicarboxylic acids were used. It was found that all the investigated binary systems have a minimum melting point on the "composition—property" graph, and this corresponds to the mixture containing about 60% of the component having the longer molecule [1,2]. When the melting points of single-component polyamides are plotted against the percentage content of amide groupings, the straight line $\underline{y} = 7\underline{x} + 110$ is obtained ($\underline{y}$ is the melting point and $\underline{x}$ is the mole percentage of hydrogen bonds) [1, 11]. It was found possible, on the basis of this equation, to determine the extent of hydrogen bonding occurring between the macromolecules of a mixed polyamide.

An examination of the mechanism of the formation of mixed polyamides for the case in which one component is 6-caprolactam led to the conclusion that in the first stage simultaneous reactions occur: polymerization of 6-caprolactam by the "hydrolytic-polymerization" mechanism, and polycondensation of the 1,6-hexanediamine salt of the dicarboxylic acid. In the last stage of the process the main direction of the reaction is the polycondensation of polyamide macromolecules formed earlier [2].

The present paper gives the results of an investigation on binary systems in which one component is an aromatic diamine. In order to determine the effect of the presence of an aromatic nucleus on the properties of the polyamide, we have investigated certain binary systems: those derived from one dicarboxylic acid and two diamines (one aliphatic and one aromatic), those derived from two acids and one diamine (aromatic), and finally those derived from two acids and two diamines (one aliphatic and one aromatic). Systems of the first type were prepared from adipic acid, 1,6-hexanediamine, and one of the following aromatic diamines: o-, m-, and p-phenylenediamines and toluene-2,4-diamine. A system of the second type was prepared from sebacic acid, 1,6-hexanediamine, and m-phenylenediamine *. As an example of systems of the third type, polyamides based on adipic and sebacic acids, 1,6-hexanediamine, and m-phenylenediamine were prepared. In addition to these, two multicomponent systems were investigated. Each was based on adipic and sebacic acids, 6-caprolactam, and 1,6-hexanediamine taken in differing but definite proportions, and the adipic or sebacic salt, respectively, of m-phenylenediamine was added in varying amount.

EXPERIMENTAL

Starting Materials

The aromatic diamines were purified by two vacuum distillations in presence of 5-10% by weight of caustic soda, and they were used immediately in the reaction. As aromatic diamines do not give salts with aliphatic dicarboxylic acids, the aromatic diamine and the dicarboxylic acid were taken separately in equivalent amounts.

The following substances were used: toluene-2,4-diamine, b.p. 166° (22 mm) and 175° (28 mm), m.p. 99° (the literature [3] gives b.p. 280° and m.p. 98°); o-phenylenediamine, b.p. 134-136° (3 mm) and 154-156° (6 mm), m.p. 102° (the literature [4, 5] gives b.p. 252-256° and m.p. 102-103.8°); m-phenylenediamine, b.p. 146° (22 mm) and m.p. 62° (the literature [4] gives b.p. 287° and m.p. 62.8°); p-phenylenediamine, b.p. 168° (37 mm) and 267° (atmospheric pressure), m.p. 140° (the literature [6] gives b.p. 267° and m.p. 142° [4]). The characteristics of the remaining monomers and the purification procedures are given in a previous paper [2].

Experimental Procudure

The reactants were introduced into the reaction tubes, which were then evacuated repeatedly and filled with nitrogen in order to remove air as completely as possible and to avoid oxidation of the aromatic amines. In other respects the apparatus, the method of carrying out the reactions, and the methods of determining the properties of the products were as described previously [1,2]. An attempt to prevent contact with air by introducing paraffin into the reaction tubes was not successful. It was thought that paraffin, being of low density, would float on the polyamide and isolate the reaction mass from the air, but it was found that the paraffin readily mixed with the molten polyamide, which formed a spongy mass when cold; also, the paraffin evaporated away to some extent.

---

* This system is actually of the first type. No example of the second type of system is discussed in this paper. —Publisher.

TABLE 1

Softening and Melting Points in the System AH-AT

Sample No.	Softening point (°C)	Melting point (°C)
2	110	190-195
3	98	130-133
4	98	128-130
5	115	150-153
6	150	175-178

The products had extended melting ranges. Softening began considerably before the melting point was reached, this point being defined as the temperature at which it becomes possible to draw the substance out into a thread. For comparison purposes softening and melting points are given in Table 1 for products of the system (adipic acid + toluene-2,4-diamine) + 1,6-hexanediamine adipate; in the other tables the figures given are melting points.

Results

Table 2 gives the melting points of the binary polyamides that we prepared.

The products were brittle yellow solids. As the content of aromatic diamine increased, the color deepened from cream or light yellow, in polyamides containing 0.2 of a molecular proportion, to amber brown, in polyamides containing 0.8 of a molecular proportion. At the same time the clarity increased, the products containing up to 0.2 of a molecular proportion of aromatic diamine being opaque, and the remainder quite transparent. All these products gave threads, though those containing more than 0.2 of a molecular proportion of aromatic diamine gave weak, brittle threads; they did not form films.

These polyamides dissolved when heated with cresol, but were insoluble in other organic solvents. Only the system AH-SmP gave some products — those having the lowest melting points — which were soluble in a mixture of alcohol and chloroform, in alcohol, and in 2-methoxyethanol (the solvents are placed in order of diminishing solvent power); they were insoluble in 2-ethoxyethanol.

TABLE 2

Melting Points of Polyamides Prepared from Mixtures Containing Aromatic Diamines

Ratio of original substances*	Original substances **					
	AH/AT	AH/ApP	AH/AoP	AH/AmP	AH/SmP	SH/SmP
1.0/0.0	250-252	250-252	250-252	250-252	250-252	210-212
0.8/0.2	190-195	225-233	205-215	200-210	170-175	150-160
0.6/0.4	130-133	185-195	150-160	170-178	110-115	110-115
0.4/0.6	128-130	136-142	115-125	135-142	115-120	90-100
0.2/0.8	150-153	125-133	90-105	133-140	125-130	85-98
0.0/1.0	175-176	260-262	105-110	258-259	145-150	145-150

We then investigated the effect of additions of various amounts of m-phenylenediamine, together with adipic or sebacic acid, to the ternary mixed polyamide prepared from AH, SH, and 6-caprolactam, two variants of this being used. The first polymer (P_1) was obtained from 40% of AH, 20% of SH, and 40% of 6-caprolactam (by weight). The second polymer (P_2) was prepared from 40% of AH, 40% of SH, and 20% of 6-caprolactam.

The first polymer melted at 145°, and the second at 160°. They were both readily soluble when heated with 85-96% alcohol, and the 15% solutions obtained did not gel in the course of 10-24 hours. P_1 and P_2 were white horny products.

---

* The numerator and denominator are the molecular proportions of the substances in the numerator and denominator, respectively, of the "fractions" at the heads of columns under the heading "Original substances".

** A — Adipic acid; H — 1,6-hexanediamine; S — sebacic acid; T — toluene-2,4-diamine; pP — p-phenylenediamine; oP — o-phenylenediamine; mP — m-phenylenediamine.

The original mixtures were prepared so that they contained 5, 10, 20, 40, 60, and 80% by weight of the mixture equivalent to 1,6-hexanediamine adipate or sebacate. The polycondensation was carried out for six hours at 250° The melting points of the products are given in Table 3.

TABLE 3

Melting Points of Four-Component Mixed Polyamides Containing an Aromatic Component

Ratio of original substances * *	Original substances *			
	$\frac{AmP}{P_1}$	$\frac{SmP}{P_1}$	$\frac{AmP}{P_2}$	$\frac{SmP}{P_2}$
1.0/0.0	258-259	145-150	258-259	145-150
0.8/0.2	130-136	95-100	130-137	100-104
0.6/0.4	96-104	78-85	110-114	85-92
0.4/0.6	90-96	70-76	105-108	80-86
0.2/0.8	105-110	88-93	130-136	90-97
0.1/0.9	125-130	105-110	145-150	115-121
0.05/0.95	155-160	–	–	120-125
0.0/1.0	145-147	145-147	160-162	160-162

The products were yellow solids. Their solubilities were lower than those of the original mixed polyamides P_1 and P_2; thus, a 15% alcoholic solution of the polyamide P_1 did not gel after 24 hours, whereas a 10% solution of the product containing only 10% of "m-phenylenediamine adipate" gelled as soon as it was cold. As Fig. 1 shows, the solubility falls regularly as the m-phenylenediamine content rises. Polyamides containing more than 60% of the m-phenylenediamine salt are no longer soluble in alcohol. All these products are somewhat more soluble in a mixture of ethanol and chloroform, but again the solubility falls as the m-phenylenediamine content rises, and it finally approaches zero. These polyamides are more readily soluble in cresol, and, whereas heat must be applied in order to dissolve them in alcohol, they are already soluble in the cold in cresol. However, with increase in the m-phenylenediamine content, the solubility again falls.

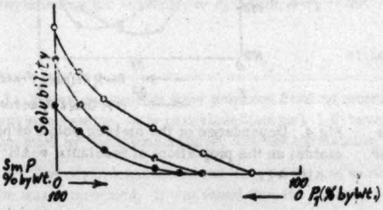


Fig. 1. Relative solubilities in various solvents of mixed polyamides of the system $P_1 - SmP$: o – mixture of ethanol and chloroform; ● – ethanol; ● – methoxyethanol

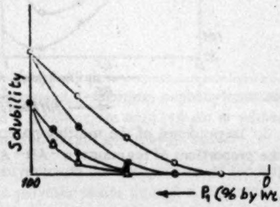


Fig. 2. Dependence of the solubilities of polyamides of various systems in ethanol on the content of the aromatic component: o – $P_1 + SmP$; ● – $P_1 + AmP$; ● – $P_2 + SmP$; Δ – $P_2 + AmP$

The solvents may be placed in the following order of diminishing solvent power: cresol, 2 : 1 mixture of ethanol and chloroform, ethanol, 2-methoxyethanol, 2-ethoxyethanol; These polymers are insoluble in chloroform, cyclohexanone, and benzene. Fig. 1 shows the dependence of the solubility of polyamides of the system $P_1 - SmP$ (in ethanol, in a mixture of ethanol and chloroform, and in 2-methoxyethanol) on the m-phenylenediamine content. Polyamides into which m-phenylenediamine was introduced in association with sebacic acid are somewhat more soluble than those in which the diamine was associated with adipic acid (Fig. 2).

---

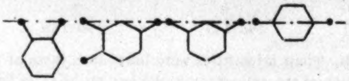
* P_1 – a mixture of AH (40%), SH (20%), and 6-caprolactam (40%); P_2 – a mixture of AH (40%), SH (40%), and 6-caprolactam (20%).

* * The numerator and denominator are the proportions by weight of the substances in the numerator and denominator, respectively, of the "fractions" at the heads of columns under the heading "Original substances".

DISCUSSION OF RESULTS

The various series of mixed polyamides that we prepared from components that include an aromatic diamine show points of resemblance to the previously described purely aliphatic polyamides. Thus, mixed polyamides having aromatic components generally have lower melting points than the corresponding single-component polyamides, as can be seen from Figures 3, 4, and 5, in which the dependence of melting point on composition is given for the systems AH–AmP, AH–AoP, AH–AmP, AH–AT, AH–SmP, SH–SmP. The same can be seen also from Figures 6 and 7, in which the dependence of melting point on the ratio of the amount of the m-phenylenediamine salt to the total amount of the remaining three components is given for the systems P_1–AmP, P_1–SmP, P_2–AmP, P_2–SmP.

With increase in the content of aromatic component the melting point of the polyamide gradually falls, passes through a minimum at a definite content of this component, and then rises again. The minimum melting point is found at different compositions in different systems, and no definite law could be found. The cause of this is evidently to be found in the different structures of the original aromatic diamines. The greatest lowering of melting point is given by o-phenylenediamine, and toluene-2,4-diamine, m-phenylenediamine, and p-phenylenediamine follow in order of reducing effect. This is to be associated, of course, with the differences in structure of these diamines.



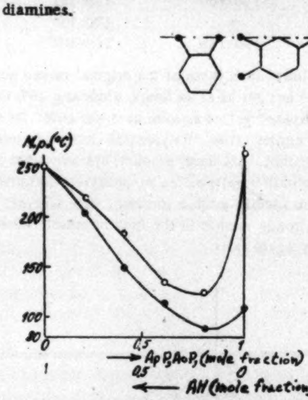


Fig. 3. Dependence of the melting points of polyamides on the proportions of reactants: o–AH–ApP; ●–AH–AoP

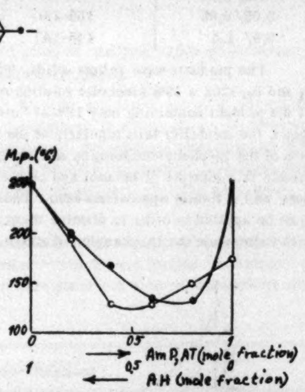


Fig 4. Dependence of the melting points of polyamides on the proportions of reactants: ●-AH–AmP; o-AH–AT.

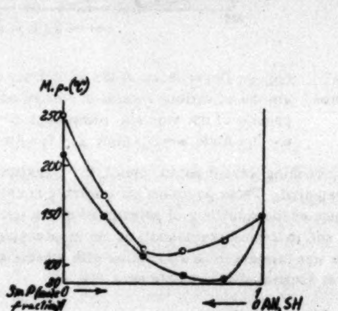


Fig. 5. Dependence of the melting points of polyamides on the proportions of reactants: o- AH–SmP; ●-SH–SmP

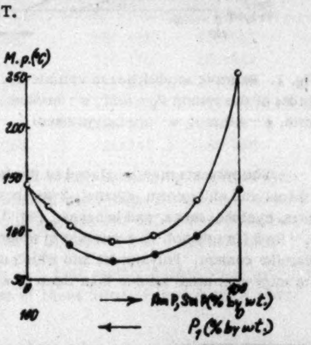


Fig. 6. Dependence of the melting points of polyamides on the contents of m-phenylenediamine adipate and of m-phenylenediamine sebacate: o- P_1–AmP; ●-P_1–SmP

The aromatic system in o-phenylenediamine, and to a lesser extent in m-phenylenediamine and in toluene-2,4-diamine, hinders the mutual approach of the polymer chains and makes it difficult for them to take up an ordered arrangement, so that the melting point is lowered. In toluene-2,4-diamine the volume of the aromatic system is increased owing to the presence of the methyl group. Unlike the purely aliphatic systems, all the investigated systems having aromatic components show no correlation between solubility and melting point. It is possible that this is associated with the formation of cross links and transformation into three-dimensional polymers.

The introduction of aromati nuclei into a polyamide molecule generally yields products of appreciably higher melting point than the corresponding purely aliphatic polyamides. Table 4 gives the melting points of polyamides formed by sebacic acid with aromatic and aliphatic diamines having equal numbers of carbon atoms in the chain.

TABLE 4

Melting Points of some Polyamides of Sebacic Acid

Diamine	M.p. (°C)	Literature reference
Benzidine	375	7
1,8-Octanediamine	197	8
α,α'-Bi-p-toluidine	360	9
1,10-Decanediamine	194	8

A similar result is obtained when the aromatic nucleus is a part of the structure of the acid, as can be seen by comparing the melting point of polyhexamethyleneterephthalamide (400° [10]) with that of polyhexamethyleneadipamide (250°).

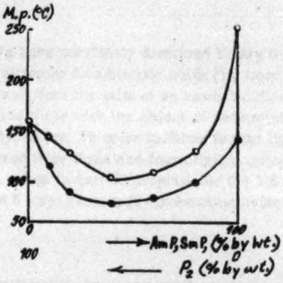


Fig. 7. Dependence of the melting points of polyamides on the contents of m-phenylenediamine adipate and of m-phenylenediamine sebacate: o- P_2 – AmP; ● - P_2 – SmP

SUMMARY

1. Mixed polyamides were prepared from an aromatic diamine (toluene-2,4-diamine, o-phenylenediamine, m-phenylenediamine, or p-phenylenediamine), 1,6-hexanediamine, and a dicarboxylic acid (adipic or sebacic), and also from m-phenylenediamine, 1,6-hexanediamine, 6-caprolactam, and adipic and sebacic acids.

2. The dependence of the melting points and solubilities of the polymers on the composition of the original mixture was determined. It was found that the melting point of a mixed polymer passes through a minimum.

LITERATURE CITED

[1] V. V. Korshak and T. M. Frunze, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No.1, 163.*

[2] V. V. Korshak and T. N. Frunze, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No.2, 372.**

[3] S. A. Mahood, P. V. L. Schaffner, Org. Synth. 11, 32 (1931).

[4] N. V. Sidgwick, J. A. Neill, J. Am. Chem. Soc. 123, 2813 (1923).

[5] Ch. A. Kraus, G. F. White, J. Am. Chem. Soc. 45, 774 (1923).

[6] Callam, Henderson, J. Soc. Chem. Ind. 38, 409 (1919).

[7] V. V. Korshak and S. R. Rafikov, J. Gen. Chem. 14, 974 (1944).

[8] D. D. Coffman, G. J. Berchet, W. R. Peterson, E. W. Spanagel, J. Polymer Science 2, 306 (1947).

[9] V. V. Korshak and S. V. Rogozhin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1951, No 5, 593.

---

* See Consultants Bureau Translation, p. 143.

** " " " " p. 333.

[10] O. B. Edgar, R. Hill, J. Polymer Science, 8, I (1952).

[11] V. V. Korshak, T. M. Frunze, Proc. Acad. Sci. USSR, 97, 261 (1954).

MACROMOLECULAR COMPOUNDS

COMMUNICATION 75. DEPENDENCE OF THE PROPERTIES OF POLYAMIDES ON THE EXTENT OF INTERMOLECULAR HYDROGEN BONDING

V. V. Korshak and T. M. Frunze

We have previously described binary mixed polyamides derived from the salts formed by 1,6-hexanediamine with two different dicarboxylic acids [1], from 6-caprolactam and the 1,6-hexanediamine salt of a dicarboxylic acid [2], and from the salts of an aromatic diamine and 1,6-hexanediamine with various dicarboxylic acids; we have studied these with the object of determining the effect of the extent of hydrogen bonding on the properties of the polyamides. In order to throw further light on the effect of this factor on the properties of polyamide systems derived from three and four original components, we have prepared mixed polyamides from the following reactants, taken in various proportions: the 1,6-hexanediamine salts of succinic, adipic, azelaic, and sebacic acids, and 6-caprolactam (2-oxohexamethylenimine).

EXPERIMENTAL

Descriptions have already been given of the purification of the starting materials and their properties [1-3], and also of the methods of performing the polycondensation reaction and of determining the properties of the products [1]. One of the systems investigated (AdH–SebH–C) has been studied also by Catlin, Czerwin, and Willey [4]. Our results for this system are in complete accord with the results obtained by these authors.

In the systems that we investigated we prepared polyamides from various proportions of reactants, and we characterized these products as in previous investigations: we determined the molecular weight, the solubility in various solvents, and the melting point. After polycondensation for six hours the molecular weights of the products were in the region of 17,000. White horny products were obtained which were sometimes quite transparent and extremely strong. They all gave fibers and films from the melt, and these could be cold-drawn; some of them gave transparent films from solution.

The solubilities of polyamides of this group are greatly dependent on composition and are generally higher than those of the products described previously. Their melting points are as high as, or even higher than, those of the binary products. It is evident that, when comparisons are made between systems of mixed polyamides differing in the number and kinds (aliphatic or aromatic) of component reactants, it is no longer possible to draw an exact parallel between melting point and solubility, as we have done previously [1,2].

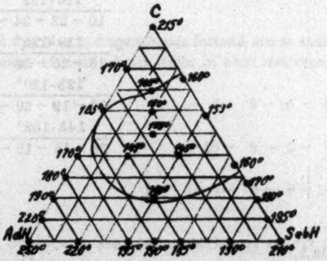


Figure 1. Variation of the melting points of polyamides of the system AdH–SebH–C; —— m.p. 165°.

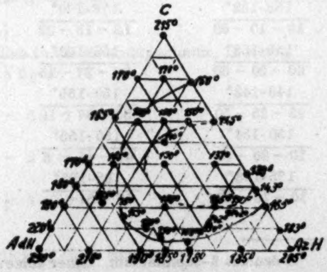


Figure 2. Variation of the melting points of polyamides of the system AdH–AzH–C; —— m.p. 160° --- m.p. 145°

TABLE 1

Dependence of the Melting Point of a Mixed Polyamide Prepared from 1,6-Hexanediamine Salts of Dicarboxylic Acids on the Proportions of Reactants

AdH – AzH – SebH	AdH – AzH – SebH	AdH – AzH – SebH	SucH – AdH – SebH	SucH – AdH – AzH
200-204° 60 – 20 – 20	158-161° 25 – 50 – 25	155-161° 17 – 51 – 32	200-206° 43 – 0 – 57	190-195° 44 – 0 – 56
172-176° 40 – 20 – 40	180-183° 10 – 60 – 30	165-170° 36 – 53 – 11	190-195° 43 – 10 – 47	167-173° 44 – 10 – 46
175-179° 20 – 20 – 60	190-193° 10 – 80 – 10	165-167° 30 – 34 – 36	180-186° 44 – 20 – 36	165-170° 45 – 20 – 35
190-195° 50 – 40 – 10	170-175° 46 – 21 – 33	165-167° 33(3) – 33(3) – 33(3)	180-184° 44 – 30 – 26	170-175° 45 – 31 – 24
165-174° 30 – 40 – 30	170-174° 17 – 30 – 53	180-184° 46 – 43 – 11	190-195° 36 – 52 – 12	
162-166° 30 – 60 – 10	175-179° 36 – 10 – 54	175-178° 46 – 32 – 22	205-210° 47 – 53 – 0	
170-174° 20 – 60 – 20	165-170° 9 – 50 – 41	180-184° 45 – 11 – 44		

1. Abbreviations: H – 1,6-hexanediamine, Ad – adipic acid, Az – azelaic acid, Seb – sebacic acid, Suc – succinic acid.

2. The numerators of the "fractions" are the melting points of the polyamides. The denominator of a "fraction" gives the relative amounts (as percentages) of the reactants in the order in which they are given at the top of the column.

TABLE 2

Dependence of the Melting Point of a Mixed Polyamide Prepared from 6-Caprolactam on the Proportions of Reactants*

AdH – AzH – C	AdH – AzH – C	AdH – SebH – C	AdH – SebH – C	AdH – AzH – SebH – C
175-178° 60 – 20 – 20	150-155° 12 – 68 – 20	158-162° 20 – 60 – 20	160-165° 40 – 40 – 20	120-125° 26 – 30 – 32 – 12
145-148° 40 – 40 – 20	142-147° 22 – 64 – 14	145-148° 40 – 40 – 20	145-148° 40 – 20 – 40	140-144° 20 – 47 – 24 – 9
140-144° 20 – 60 – 20	142-147° 26 – 62 – 12	145-149° 60 – 20 – 20	145-150° 20 – 40 – 40	140-143° 19 – 43 – 20 – 18
165-169° 50 – 10 – 40	150-155° 31 – 60 – 9	115-118° 10 – 50 – 40	155-160° 25 – 25 – 50	145-150° 31 – 36 – 19 – 14
130-133° 30 – 30 – 40	168-172° 39 – 57 – 4	130-134° 30 – 30 – 40	160-164° 20 – 20 – 60	130-134° 17 – 40 – 21 – 22
137-140° 10 – 50 – 40	180-190° 70 – 0 – 30	110-113° 50 – 10 – 40	165-170° 15 – 15 – 70	148-150° 29 – 34 – 18 – 19
158-162° 30 – 10 – 60	176-170° 63 – 15 – 22	120-125° 10 – 30 – 60		110-115° 19 – 23 – 24 – 34
155-158° 20 – 20 – 60	155-160° 58 – 27 – 15	140-144° 20 – 20 – 60		110-115° 25 – 25 – 25 – 25
140-143° 25 – 25 – 50	150-155° 53 – 37 – 10	115-119 25 – 25 – 50		125-130° 17 – 19 – 20 – 44
150-154° 10 – 30 – 60	150-155° 49 – 46 – 5	140-143° 30 – 10 – 60		145-152° 26 – 15 – 15 – 44
175-178° 10 – 10 – 80	185-195° 46 – 54 – 0	170-174° 10 – 10 – 80		

---

*C denotes 6-caprolactam. Other abbreviations are as in Table 1.

The melting points of the products obtained are given in Tables 1 and 2.

DISCUSSION OF RESULTS

Ternary diagrams showing the dependence of melting point on composition for mixed polyamides are given in Figures 1, 2, 3, and 4 for the systems AdH – SebH – C, AdH – AzH – C, AdH – AzH – SebH, and AzH – SebH – C. It will be readily seen that the polyamides of lowest melting point lie nearest to the center of the triangle. If, however, a particular component predominates, the polyamide is further from the center of the triangle and has a higher melting point. Constant melting point isotherms are displaced in the direction of the side of the triangle representing the system having the lowest melting points. It is clear that in ternary systems the derangement of structure and the obstacles in the way of hydrogen bonding are still greater than in the binary systems studied previously [1, 2, 3].

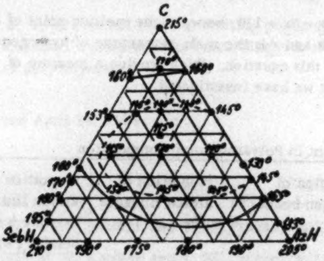


Figure 3. Variation of the melting points of polyamides of the system AzH – SebH – C; ——— m.p. 160°; ------- m.p. 145°.

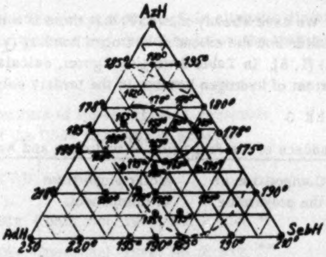


Figure 4. Variation of the melting points of polyamides of the system AdH – AzH – SebH; ——— m.p. 165° --------m.p. 185°.

When we consider the possibilities of hydrogen bonding in the system AdH – SebH – C (1 : 1 : 1) for the following three chain structures:

– Ad – H – Seb-H — C — Ad — H — Seb - H — C —

– Seb - H – Ad –H — C — Seb – H — Ad — H — C —

– C — Ad –H –Seb - H — Ad — H — Seb – H — C —

we find that the hydrogen bonds formed are as indicated by the dotted lines in the following scheme, in which the number of main-chain atoms in each monomer unit is expressed by a figure:

– 6 – 8 – 10 – 8 – 7 – 6 – 8 – 10 – 8 – 7 –

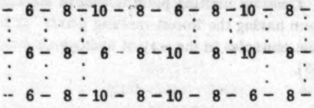
– 10 – 8 – 6 – 8 – 7 – 10 – 8 – 6 – 8 – 7 –

– 7 – 6 – 8 – 10 – 8 – 6 – 8 – 10 – 8 – 7 –

On the other hand, considering the binary system AdH – SebH for the following chain structures:

— Ad — H — Seb - H — Ad — H — Seb — H —
—Ad — H — Ad — H — Seb - H — Seb —H —
— Ad — H— Seb - H — Seb - H — Ad —H —

we find that the hydrogen bonding will be as indicated in the following scheme:



It is evident that in the second polymer the proportion of amide groupings that participate in intermolecular hydrogen bonding will be considerably greater than in the first.

We have already shown [1] that there is a linear relationship, $y = 7x + 110$, between the melting point of a polyamide and the extent of hydrogen bonding (y is the melting point and x is the mole percentage of hydrogen bonds) [1, 5]. In Table 3 we give figures, calculated with the aid of this equation, which provide a measure of the extent of hydrogen bonding in the ternary polyamide systems that we have investigated.

TABLE 3

Dependence of the Proportion of Hydrogen and Amide Linkages present in Polyamides on Composition

Composition of the polyamide	Molar proportions of components	M.p. (°C)	Proportion of hydrogen bonds (%)	Proportion of amide linkages (%)	Proportion of the amide linkages that are hydrogen-bonded (%)
AdH	–	250-252	20.0	20.0	100.0
AzH	–	205-207	13.6	15.4	88.3
SebH	–	210-212	14.3	14.3	100.0
C	–	215-217	15.0	20.0	75.0
AdH – SebH	2 : 3	185-187	10.7	16.1	66.4
AdH – AzH	2 : 3	178-180	9.7	16.9	57.4
AzH – SebH	2 : 3	170-173	8.5	14.7	57.7
AzH – C	2 : 3	130-132	3.0	17.0	17.6
SebH – C	1 : 4	153-155	6.1	17.6	34.6
AdH – AzH – C	1.1 : 1 : 3.56	130-123	2.8	19.0	14.7
AdH – SebH – C	1 : 1.6 : 4.6	145-150	5.0	17.6	28.4
AdH – SebH – C	2.4 : 1 : 5.6	145-148	5.0	18.6	27.4
AdH – SebH – C	1.2 : 1 : 1.3	160-162	7.1	17.5	40.5
AdH – SebH – C	1.1 : 1 : 1 : 8.4	160-164	7.1	18.1	39.2

It can be seen from Table 3 that a considerable proportion of the amide groupings present in mixed polyamides is not linked by hydrogen bonds to the amide groupings of neighboring macromolecules. Such amide groupings have no effect on the melting point and other properties of the mixed polyamides. Confirmation of this inference can be found in the fact that the melting points of polyamides derived from 1,6-hexanediamine and dicarboxylic acids having odd numbers of carbon atoms in their molecules do not fall on the graph when it is assumed that all their amide groupings are hydrogen-bonded. Owing to the operation of steric factors, hydrogen bonds can be formed by only a part of the amide groupings of such polyamides, thus accounting for the observed discrepancy.

The results now obtained also confirm another of the conclusions reached in our earlier work [1], namely, that no polyamide derived from straight-chain aliphatic diamines and dicarboxylic acids, and having no alkyl side groups, other substituents, or hetero atoms, can have a melting point below that of polyethylene, i.e., 110°. The results provide further new material confirming the correctness of a conclusion that we reached previously, namely, that there is a direct relationship between the melting points of mixed polyamides and the extent to which hydrogen bonding occurs in these polymers.

SUMMARY

1. An investigation was made of the dependence of the melting points of ternary and quaternary polyamides on their quantitative composition, the reactants in the systems studied being the 1,6-hexanediamine salts of succinic, adipic, azelaic, and sebacic acids and 6-caprolactam, taken in various proportions.

2. The extent to which hydrogen bonding occurs in these polymers was calculated.

3. It was proved that the melting points of mixed polyamides derived from straight-chain aliphatic diamines and dicarboxylic acids and not containing side chains, substituents, or hetero atoms cannot be below the melting point of polyethylene.

Received April 14, 1954

Institute of Heteroorganic Compounds
of the USSR Academy of Sciences

LITERATURE CITED

[1] V. V. Korshak and T. M. Frunze, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 1, 163. *

[2] V. V. Korshak and T. M. Frunze, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 2, 372. **

[3] V. V. Korshak and T. M. Frunze, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 3, 551. ***

[4] W. E. Catlin, E. P. Czerwin, R. H. Willey, J. Polymer Science, 2, 412 (1947).

[5] V. V. Korshak and T. M. Frunze, Proc. Acad. Sci. USSR, 97, 261 (1954).

---

* See Consultants Bureau Translation, p. 143.

** " " " " p. 333.

*** " " " " p. 487 this issue.

BLANK
PAGE

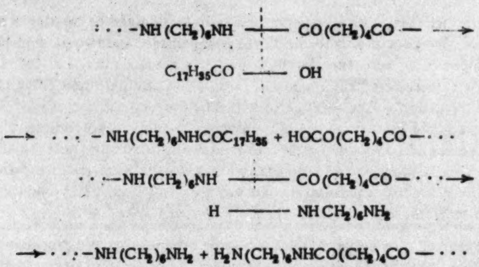
MACROMOLECULAR COMPOUNDS

COMMUNICATION 76. ROLE OF EXCHANGE REACTIONS IN POLYAMIDE FORMATION

V. V. Korshak and T. M. Frunze

It was shown long ago by one of us in collaboration with Rafikov [1], Pinkina [2], and Zamyatina [3] that exchange reactions occur between polyamide macromolecules and the substances of low molecular weight from which they are prepared, such as mono- and di-carboxylic acids and diamines. Such exchange reactions are degradative, and they result in the breakdown of the polyamide macromolecule, either by acidolysis – by reaction with a dicarboxylic acid – or by aminolysis – by reaction with a diamine. The regularities to be observed in these reactions were studied by one of us in collaboration with Zamyatina [3], the example taken being polyhexamethyleneadipamide, which was subjected to acidolysis by adipic and stearic acids and to aminolysis by 1,6-hexanediamine.

Acidolysis and aminolysis are reactions in which the active carboxyl or amino group of the acid or amine taken reacts with the amide grouping of the polymer in the following manner:



$$\begin{array}{ccc} \cdots\text{–NH(CH}_2)_6\text{NH} & \text{—}\vdots\text{—} & \text{CO(CH}_2)_4\text{CO}\text{ — } \longrightarrow \\ \text{C}_{17}\text{H}_{35}\text{CO} & \text{—}\vdots\text{—} & \text{OH} \end{array}$$

$$\longrightarrow \cdots\text{–NH(CH}_2)_6\text{NHCOC}_{17}\text{H}_{35} + \text{HOCO(CH}_2)_4\text{CO}\text{—}\cdots$$

$$\begin{array}{ccc} \cdots\text{–NH(CH}_2)_6\text{NH} & \text{—}\vdots\text{—} & \text{CO(CH}_2)_4\text{CO}\text{—}\cdots\longrightarrow \\ \text{H} & \text{———} & \text{NHCH}_2)_6\text{NH}_2 \end{array}$$

$$\longrightarrow \cdots\text{–NH(CH}_2)_6\text{NH}_2 + \text{H}_2\text{N(CH}_2)_6\text{NHCO(CH}_2)_4\text{CO}\text{—}\cdots$$

It was found that the extent to which the polyamide was degraded was proportional to the amount of acid or amine used.

The investigation of several different polyamide systems has shown that amidolysis exchange reactions can occur between amide groupings [13, 14], and one of us in collaboration with Vinogradova [4,5], and also with Kursanov and Vinogradova [6], has shown that a similar, esterolysis exchange reaction can occur between two ester groupings, both in polyesters and in esters of low molecular weight.

The important part played by exchange reactions in the process of polyamide formation is evidenced also by the results of an investigation of the reaction between 2-aminoethanol and sebacic acid carried out by one of us in collaboration with Chelnokova and Distler [7]. It was shown that in the course of the formation of the polyamidoester extensive rearrangement of the monomer units of the macromolecule occurred.

It was shown by one of us in collaboration with Bresler, Pavlova, and Finogenov [8] that the interaction of two polyamide fractions of different molecular weights yields a polyamide whose molecular weight is between those of the original fractions, which proves that a state of polycondensational equilibrium is attained in reactions between polyamide macromolecules. However, prior to the present investigation we had not obtained direct proof of the occurrence of such exchange reactions between polyamide macromolecules as could bring about a considerable measure of exchange of monomer units between the macromolecules and the "leveling out" of their compositions. The investigation of such reactions is of great interest for the correct understanding of the mechanism of polyamide formation and polycondensation processes in general.

In order to investigate the course and extent of such reactions we studied the behavior of polyamides of different structures when heated together in the molten condition. For this purpose we prepared two single-component polyamides – from 1,6-hexanediamine azelaate and 1,6-hexanediamine sebacate. Polyhexamethyleneazelaamide melted at 205° and was completely insoluble in ethanol and in 2-methoxyethanol. Polyhexamethylenesebacamide melted at 210° and was also insoluble in ethanol and 2-methoxyethanol.

We first determined the mutual solubilities of the molten polyamides. Bernatskaya and Kudryavstev [9] showed that polycaprolactam and polyhexamethyleneadipamide are miscible in all proportions, and it could be expected that our polyamides would behave in the same way. Mixtures of these polyamides were stirred at 250° in an atmosphere of nitrogen. It was found that they formed a homogeneous mixture in all proportions; the product was insoluble in alcohol.

A mixture obtained by melting two molecular proportions of polyhexamethyleneazelaamide with three molecular proportions of polyhexamethylenesebacamide was heated for 24 hours in cresol solution, at first at 150-180°, and for the last eight hours at 240°. The resulting polyamide melted at 180-183° and dissolved when heated with ethanol or 2-methoxyethanol. The same mixed polyamide was obtained when 15 g of polyhexamethyleneazelaamide was heated with 23.6 g of polyhexamethylenesebacamide at 240-250° in an atmosphere of nitrogen in an autoclave for 30 hours. It melted at 178-183° and dissolved when heated with ethanol or 2-methoxyethanol. A mixed polyamide of the same composition was obtained from 0.4 mole of 1,6-hexanediamine azelaate (AzH) and 0.6 mole of 1,6-hexanediamine sebacate (SH). It melted at 170-175° and dissolved when heated with ethanol or 2-methoxyethanol, i.e., was the same product as that obtained by heating the polyamides themselves. The somewhat higher melting points of the first products are evidently to be explained by incomplete attainment of equilibrium as a result of the high viscosity of the melt of the original polyamide mixture.

A further object for investigation was the three-component polyamide obtained by heating a mixture of one part of polyhexamethyleneazelaamide, one part of polyhexamethyleneadipamide, and two parts of polycaprolactam at 250-260° in an atmosphere of nitrogen in an autoclave for 30 hours. The product melted at 148-153° and dissolved when heated with ethanol or 2-methoxyethanol, whereas each of the original three polyamides was insoluble in these solvents and melted above 200°. The mixture obtained by melting the above mixture of polyamides melted at 240-250° and was insoluble in ethanol and in 2-methoxyethanol. A polyamide of the same composition prepared from 1,6-hexanediamine adipate (AdH), 1,6- hexanediamine azelaate (AzH), and 6-caprolactam (1 : 1 : 2) melted at 140-143° and dissolved when heated with ethanol or 2-methoxyethanol, i.e., was the same product as that obtained by heating the polyamides themselves and was greatly different in properties from the mixture formed when the polyamides were melted together.

We have therefore succeeded in proving that polyamides of the same composition and properties can be prepared both directly from the appropriate monomeric substances (diamine salts of dicarboxylic acids) and by heating a mixture of polyamides, each of which is prepared beforehand from each salt separately. This statement is illustrated by the following scheme:

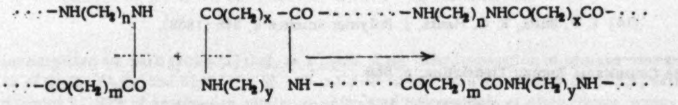
$$\begin{tikzcd}
\text{SH} \arrow[d, "-H_2O"] & + & \text{AzH} \arrow[r, "-H_2O"] \arrow[d, "-H_2O"] & \text{mixed polyamide} \\
\text{polyhexamethylenesebacamide} & + & \text{polyhexamethyleneazelaamide} \arrow[ur] &
\end{tikzcd}$$

which may be expressed also by the following equations:

$$\begin{tikzcd}[column sep=small]
xH_2N(CH_2)_6NH_2\cdot(HOOC)_2(CH_2)_8 \arrow[d, "-H_2O"'] & + & xH_2N(CH_2)_6NH_2\cdot(HOOC)_2(CH_2)_7 \arrow[r, "-H_2O"] \arrow[d, "-H_2O"] & {[-NH(CH_2)_6NHCO(CH_2)_8CONH(CH_2)_6NHCO(CH_2)_7CO-]_x} \\
{[NH(CH_2)_6NHCO(CH_2)_8CO-]_x} & + & {[-NH(CH_2)_6NHCO(CH_2)_7CO-]_x} \arrow[ur] &
\end{tikzcd}$$

The results of the above-described experiments show that, when a mixture of polyamides is heated, transamidation reactions occur, so that the macromolecules of the various single-component polyamides exchange some of their repeating units with formation of new macromolecules of a mixed polyamide, all containing the same proportions of the monomer units. It will be clear that such a result could be obtained only by the occurrence of exchange reactions between separate polyamide molecules, and the fact that this result is obtained provides a reliable proof of the occurrence of such reactions.

These exchange reactions between macromolecules contribute to the polycondensation equilibrium, and it is evident that they occur both with the end groups of the macromolecules by the acidolysis or aminolysis mechanism (see above), and also by interaction of the amide groupings of different macromolecules by the amidolysis mechanism, as follows:



$$\begin{matrix} \cdots-NH(CH_2)_nNH & & CO(CH_2)_x-CO & & \cdots\cdots-NH(CH_2)_nNHCO(CH_2)_xCO-\cdots \\ \vdots & + & \vdots & \longrightarrow & \\ \cdots-CO(CH_2)_mCO & & NH(CH_2)_y & & NH-\cdots\cdots CO(CH_2)_mCONH(CH_2)_yNH-\cdots \end{matrix}$$

We may note, incidentally, that such a leveling out of composition is very probable from the thermodynamical point of view, since random distribution of monomer units should lead to increase of entropy.

We must draw attention to another important conclusion that can be drawn from the results, namely, that it is now clear that the structure and composition of the macromolecules of mixed polyamides, and probably also polyesters, are determined in the final stage not by the kinetics of the individual elementary processes, as in the copolymerization of vinyl monomers, but by polycondensation equilibrium, which depends on the proportions of the separate monomeric reactants. This conclusion lends further emphasis to the fundamental difference that exists – in reaction mechanism, and in the laws governing the reaction – between polymerization and polycondensation processes, a fact that we have frequently pointed out in the past [10-12].

SUMMARY

1. When mixtures of different single-component polyamides were heated, mixed polyamides were formed, and these were similar to the products obtained when the appropriate mixtures of monomers were heated.

2. It was shown that exchange reactions play an important part in polycondensation processes.

3. It is considered that the structure and composition of polyamide macromolecules, and also their fractional composition, are determined not by the kinetics of the individual stages of the process, but by the state of polycondensation equilibrium.

Received April 14, 1954

Institute of Heteroorganic Compounds
of the USSR Academy of Sciences

LITERATURE CITED

[1] V. V. Korshak and S. R. Rafikov, J. Gen. Chem. 14, 974 (1944); Proc. Acad. Sci. USSR 48, 36 (1945).

[2] S. R. Rafikov, V. V. Korshak, and L. N. Pinkina, J. Gen. Chem. 14, 1003 (1944).

[3] V. V. Korshak and V. A. Zamyatina, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1945, 609.

[4] V. V. Korshak and S. V. Vinogradova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, 1109.*

[5] V. V. Korshak and S. V. Vinogradova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1951, 334.

[6] D. N. Kursanov, V. V. Korshak, and S. V. Vinogradova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, 140.**

[7] V. V. Korshak, G. N. Chelnokova, and G. I. Distler, Proc. Acad. Sci. USSR, 82, 589 (1952).

[8] S. E. Bresler, V. V. Korshak, S. A. Pavlova, and P. A. Finogenov, Proc. Acad. Sci. USSR, 87, 961 (1952).

---

* See Consultants Bureau Translation, p. 967. ** See Consultants Bureau Translation, p. 125.

[9] Ya. E. Bernatskaya and G. I. Kudryavtsev, Collection of papers, "Synthetic Fibers", 3, 88 (1952).

[10] V. V. Korshak, Chemistry of Macromolecular Compounds, Acad. Sci. USSR Press, Moscow and Leningrad, 1950, page 307.

[11] V. V. Korshak, Prog. Chem. 21, 121 (1952).

[12] V. V. Korshak, Methods of Macromolecular Organic Chemistry, Vol. 1, General Methods for Synthesis of Macromolecular Compounds, Acad. Sci. USSR Press, Moscow and Leningrad, 1953, p. 481.

[13] S. R. Rafikov, V. V. Korshak, and T. N. Chelnokova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, No. 4, 743. *

[14] L. F. Beste, R. C. Houtz, J. Polymer Science 8, 395 (1952).

---

[*] See Consultants Bureau Translation, p. 669.

BRIEF COMMUNICATIONS

CONTACT – CATALYSIS REACTIONS OF PENTANE IN PRESENCE OF A CHROME – ALUMINA – MAGNESIA CATALYST

N. I. Shuikin, E. A. Timofeeva, and V. M. Sladkikh

In a previous investigation we have shown [1] that, as a result of the dehydrogenation of pentane over a mixed catalyst consisting of Cr_2O_3, Al_2O_3, and MgO (45 : 30 : 25 mole-%) at 500° at a space velocity of 1.2, catalyzates are obtained containing 21-22% of pentenes in admixture with some hydrocarbons of other classes, including cyclopentane.

TABLE 1

Results of the Dehydrogenation of Pentane at Various Temperatures

Results of experiment	Temperature (°C)			
	450	500	527	550
Yield of catalyzate (%)	95.0	88.5	80.4	73.9
Amount of gas evolved (liters at S.T.P.)	1.00	5.50	8.75	10.05
Properties of catalyzate:				
n_D^{20}	1.3600	1.3660	1.3675	1.3700
d_4^{20}	0.6302	0.6347	0.6368	0.6382
Iodine number	33.4	73.8	85.3	94.8
Content of unsaturateds (% by weight):	9.2	20.3	23.5	26.0
(on amount of pentane passed)	8.7	17.9	18.9	19.2
Composition of gas:				
Unsaturateds	7.1	1.2	7.3	9.1
Hydrogen	65.9	79.6	78.9	78.3
Paraffins	27.0	19.2	13.8	12.6

It was of interest to determine the effect of variation of temperature on the extent of dehydrogenation of pentane and on the composition of the catalyzate. With this object we carried out experiments on the dehydrogenation of pentane at 450-550° in presence of a chrome-alumina-magnesia catalyst. In each experiment 31.3 g of pentane was brought into contact with the catalyst at a space velocity of 1.2. The results of typical experiments are given in Table 1, which shows that with rise in temperature from 450° to 550° the content of unsaturated hydrocarbons in the catalyzate increases from 9.2% to 26%.

A combined catalyzate from experiments at 550° was fractionated through a 70-plate column. The properties of the fractions obtained are given in Table 2.

INVESTIGATION OF FRACTIONS

Fraction I. By the application of the methods of bromination and precise rectification to this fraction it was established that 2-methylbutane, unchanged pentane, pentenes (the bulk of the fraction), and 1,4-pentadiene were present.

Fraction II. Judging from the value of the iodine number, this fraction contained 26.4% of pentenes in admixture with unchanged pentane. We have checked the iodine-number method on artificial mixtures of pentane and pentenes [1].

Fraction III. Like Fraction I, this was investigated by the method of preliminary bromination, and 2.3 g of it yielded 0.2 g of unchanged pentane (b.p. 35.9-38.0°), 1.2 g of dibromopentanes (b.p. 56-62°/11 mm, n_D^{20} 1.5095 and d_4^{20} 1.6820), and 1.5 g of 1, 2, 3, 4-tetrabromopentane, m.p. 114-115° [2], which indicates that, apart from pentane and pentenes, 1,3-pentadiene (piperylene) was present in this fraction.

Fraction IV. Investigation of this fraction by the Raman-spectra method * showed that it consisted mainly of cyclopentane, a result that was fully in accord with its physicochemical properties (see Table 2). In the literature [3] the following properties are reported for cyclopentane: b.p. 49.3°, n_D^{20} 1.4068 and d_4^{20} 0.7460.

TABLE 2

Properties of the Fractions of the Liquid Catalyzate Obtained in Experiments at 550°

Fraction	Boiling range (°C, corrected)	Amount (g)	Properties		
			n_D^{20}	d_4^{20}	Iodine number
I	26.5-29.0	8.2	1.3635	–	–
II	29.0-38.0	431.0	1.3635	0.6323	95.9
III	38.0-47.0	3.0	1.4140	0.6790	–
IV	47.0-52.0	2.2	1.4020	0.7410	–
V	52.0-72.5	5.0	1.3810	0.6702	26.9
VI	72.5-95.0	0.8	1.4570	–	112.3
VII	95.0-150.0	1.4	1.4845	–	44.5
VIII	150.0-200.0	1.7	1.5245	–	26.9
	Residue	1.0	–	–	–

Fraction V. After removal of unsaturated hydrocarbons by adsorption on silica gel the fraction boiled over the range 58.1-65.8° (corrected) and had n_D^{20} 1.3755 and d_4^{20} 0.6641. The presence of 2-methyl- and 3-methylpentanes was detected by the Raman-spectra method [3].

Fraction VI. Judging from the boiling range and the positive formolite test, this fraction contained benzene and other hydrocarbons.

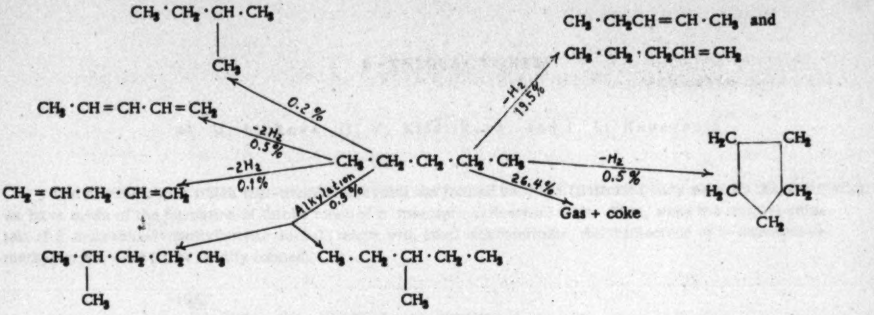
Fraction VII. Ullmann oxidation [4] of this fraction yielded benzoic acid (m.p. 120-121°) and isophthalic acid, the dimethyl ester of which melted at 63°. We thus proved that toluene and m-xylene were present in this fraction.

In the same way the presence of m-dialkylbenzenes in Fraction VIII was established, but the identity of these could not be established in detail owing to lack of material.

The results of the investigations of the fractions isolated from the catalyzate form the basis of the following scheme of the main reactions of pentane in contact with a chrome-alumina-magnesia catalyst at 550°:

---

* Analysis of the fractions by the Raman-spectra method was carried out by Yu. P. Egorov, to whom we are very grateful.


CH₃·CH₂·CH·CH₃
CH₃
CH₃·CH₂CH=CH·CH₃ and
CH₃·CH₂·CH₂CH=CH₂
0.2%
−H₂
19.5%
CH₃·CH=CH·CH=CH₂
−2H₂
0.5%
−2H₂
0.1%
CH₂=CH·CH₂·CH=CH₂
CH₃·CH₂·CH₂·CH₂·CH₃
−H₂
0.5%
26.4%
Gas + coke
H₂C
CH₂
H₂C
CH₂
CH₂
Alkylation
0.5%
CH₃·CH·CH₂·CH₂·CH₃
CH₃
CH₃·CH₂·CH·CH₂·CH₃
CH₃

We consider that benzene and its homologs were formed under our conditions as a result of the dimerization of piperylene [5], followed by redistribution of hydrogen, dehydrogenation, and dealkylation.

Thus, when the temperature of the treatment of pentane in contact with a chromei-alumina-magnesia catalyst is raised from 500° to 550°, dehydrogenation is intensified with simultaneous intensification of gas formation; small amounts of 1,3- and 1,4-pentadienes are formed.

The formation of cyclopentane by direct dehydrocyclization of pentane, which we have observed previously [1], is of fundamental interest. The formation of cyclopentane hydrocarbons as a result of the reactions of more complex paraffins – octane [6] and 2,2,4-trimethylpentane [7] – in presence of platinized charcoal (20% Pt) at 300° has been observed recently by B. A. Kazansky, A. L. Liberman, and others. We were the first to establish the possibility of the direct dehydrocyclization of pentane to cyclopentane in presence of a mixed oxide catalyst at 550°.

Received March 15, 1955

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

LITERATURE CITED

[1] E. A. Timofeeva, S. S. Novikov, and N. I. Shuikin, Proc. Acad. Sci. USSR 92, No. 2, 345 (1953).

[2] A. W. Hofmann, Ber. 14, 659 (1881).

[3] G. Egloff, Physical Constants of Hydrocarbons, N. Y., Vol. 2, 1940, p. 54.

[4] F. Ullmann, J. B. Uzbachian, Ber. 36, 1797 (1903).

[5] F. Yu. Rachinsky and M. Z. Zalmanovich, Collection of Papers on General Chemistry, Volume 1, Acad. Sci. USSR Press, Moscow and Leningrad, 1953, p. 415.

[6] B. A. Kazansky, A. L. Liberman, T. F. Bulanova, V. T. Aleksanyan, and Kh. E. Sterin, Proc. Acad. Sci. USSR, 95, No. 1, 77 (1954).

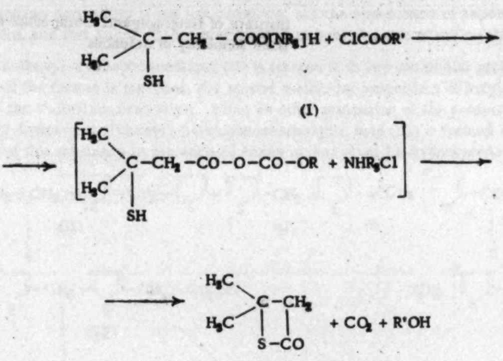
[7] B. A. Kazansky, A. L. Liberman, V. T. Aleksanyan, and Kh. E. Sterin, Proc. Acad. Sci. USSR, 95, No. 2, 281 (1954).

BLANK
PAGE

β-THIOLACTONES

M. G. Linkova, O. V. Kildisheva, and I. L. Knunyants

The readiness with which four-membered cycles are formed has been illustrated once more by the observation we have made of the formation of thiolactones of β-mercapto carboxylic acids. Thus, when the triethylamine salt of 3-mercapto-3-methylbutyric acid (I) reacts with ethyl chloroformate, the thiolactone of 3-mercapto-3-methylbutyric acid (II) is readily formed:



(I)

(II)

The substance (II) is a colorless mobile liquid having a characteristic odor that is not reminiscent of the odor of thiols. This first representative of this new class of compounds – the thiolactone of 3-mercapto-3-methylbutyric acid – is an active acylating agent: it reacted with aniline, benzylamine, and valine, the respective products being the anilide and benzylamide of 3-mercapto-3-methylbutyric acid and N-(3-mercapto-3-methylbutyryl) valine. The hydrolysis of the thiolactone of 3-mercapto-3-methylbutyric acid with water in presence of HBr yielded the original mercapto acid. When the thiolactone was heated in a sealed tube with traces of moisture, a solid linear polymer was obtained.

EXPERIMENTAL

1. A solution of 4.6 g of ethyl chloroformate in 10 ml of chloroform was added at −5° to a mixture of 5 g of the substance (I), 40 ml of chloroform, and 7 ml of triethylamine. After 30 minutes the reaction for the SH group was negative. After addition of absolute ether (100 ml) and removal of triethylamine hydrochloride (6 g), the solution was washed – first with water, then with sodium bicarbonate solution, and finally with water again – and dried with sodium sulfate. The residue after removal of solvents boiled at 33-34° (1.5 mm) and consisted of 2 g (50%) of the thiolactone of 3-mercapto-3-methylbutyric acid, d^{20}_{20} 1.0425; n^{20}_{D} 1.4865; Calculated MR 31.23; Found MR 31.9; M 109 (cryoscopically in benzene).

Found %: C 51.81; H 6.99; S 27.01

C_5H_8OS. Calculated %: C 51.72; H 6.9; S 27.58

Anilide – obtained in the form of needles (from heptane), m.p. 78-79°.

Found %: N 6.8

$C_{11}H_{15}ONS$. Calculated %: N 6.7

Benzylamide – needles (from heptane), m.p. 61-62°.

Found %: C 64.23; H 7.81; S 14.39; N 6.03
$C_{12}H_{17}ONS$. Calculated %: C 64.57; H 7.62; S 14.35; N 6.27

2. The thiolactone of 3-mercapto-3-methylbutyric acid (0.22 g) was added to a vigorously stirred solution of 0.22 g of the sodium salt of valine in 30 ml of water. After 90 minutes the solution was acidified to Congo red and filtered. The product was 0.2 g of N–(3-mercapto-3-methylbutyryl) valine in the form of colorless crystals, m.p. 122-123° (from benzene or ethyl acetate).

Found %: C 51.40; H 8.13; S 13.92; N 5.90
$C_{10}H_{19}O_3NS$. Calculated %: C 51.5; H 8.15; S 13.73; N 6.00

Received April 4, 1955

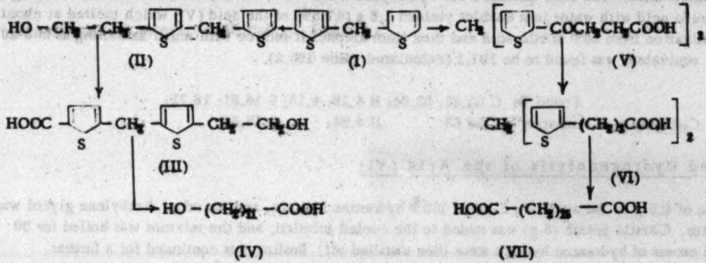
Institute of Heteroorganic Compounds of the
USSR Academy of Sciences

SYNTHESIS AND REACTIONS OF SOME 2,2'-METHYLENEDITHIOPHENE DERIVATIVES

Ya. L. Goldfarb and M. L. Kirmalova

Since 1952 one of us has been working on the hydrogenolysis of substituted thiophenes with formation of aliphatic compounds [1]. By this method we have prepared some difficultly accessible hydrocarbons, higher aliphatic alcohols, ketones, and amino acids. One of our starting materials was 2,2'-methylenedithiophene (I), from which we prepared 1,13-tridecanediol, undecyl alcohol, and decanoic acid. We also studied the preparation of aliphatic hydroxy acids and dicarboxylic acids. This part of the investigation of the hydrogenolysis of thiophene derivatives is not yet complete, but the appearance of papers by Badger and coworkers [2] and by Buu-Hoi and Dat Xuong [3] has prompted us to publish some of our results.

When 5-thenyl-2-thiopheneethanol (II) is treated with two molecular proportions of butyllithium, the α-hydrogen of the former is replaced, the second molecular proportion of butyllithium being required for the formation of the O-lithium derivative. When an ether suspension of the product is mixed with solid carbon dioxide, 5-[(2-hydroxyethyl)thenyl]-2-thiophenecarboxylic acid (III) is formed in a yield of about 32%. Hydrogenolysis of this substance in presence of Raney nickel gives 12-hydroxydodecanoic acid (IV) in high yield.



Acylation of (I) with succinic anhydride in nitrobenzene in presence of aluminum chloride, or with the acid chloride of the monomethyl ester of succinic acid in benzene or heptane in presence of stannic chloride, yields 3,3'-(5,5'-methylenedithenoyl)dipropionic acid (V) (29% and 47% yield, respectively). The crude acid is very much contaminated with resin, and this is difficult to remove. The best method of purification is crystallization from water, but owing to the low solubility of the acid it is necessary to work with very large volumes or to carry out long extractions in a Soxhlet. After separation from aqueous solution, the acid requires still further purification.

By reduction of the acid (V) by a modification of Kizhner's method [4], we obtained 5,5'-methylenedi-2-thiophenebutyric acid (VI), and hydrogenolysis of this yielded heptadecanedioic acid (VII). We were unable to isolate this acid from the reaction mixture in the usual way, because it was strongly adsorbed by the catalyst. The catalyst was therefore dissolved in excess of hydrochloric acid, and the acid (VII) was extracted from the resulting mixture with ether. It is probable that only part of the acid formed passed into the ether, for, after purification it was found to be insoluble, not only in ether, but also in benzene, chloroform, etc.

EXPERIMENTAL

Preparation and Hydrogenolysis of the Acid (III)

1. A solution of 0.03 mole of butyllithium in ether was added at −5° to 0° to a solution of 0.015 mole (3.5 g) of the alcohol (II) in 30 ml of dry ether. The mixture was stirred for 15 minutes and then poured into a mixture of dry ice and ether. The precipitate then formed was dissolved in water, and the aqueous layer was separated from the ether layer and acidified, when 1.3 g (32%) of the acid (III) separated; m.p. 106.5-107.5° (from water).

After recrystallization from 50% acetic acid and then from 50% aqueous alcohol the melting point was raised to 110.5-111°. The neutralization equivalent was found to be 267.1 (calculated value 268.35).

Found %: C 53.75; 53.71; H 4.35; 4.49; S 23.81; 24.16

$C_{12}H_{12}O_3S_2$. Calculated %: C 53.71 H 4.51 S 23.90

From the ether layer 1.7 g (48%) of the substance (II) was recovered.

2. A solution of 2 g of the acid (III) in 30 ml of 10% sodium carbonate solution was mixed with 180 ml of water and with Raney nickel [5] prepared from 70 g of a 30% alloy and subsequently washed with ten successive 500-ml portions of distilled water. The mixture was stirred at 90° for 90 minutes. The catalyst was filtered off and washed with 5% sodium carbonate solution. The alkaline solution was poured into 1:1 hydrochloric acid, and 1.5 g (94%) of the acid (IV), m.p. 78-78.5°, separated. The melting point was raised to 83-83.5° by recrystallization from a mixture of ethyl acetate and petroleum ether; the literature gives 83-84° [6] and 84-85° [7]. The neutralization equivalent was found to be 216.1 (calculated value 216.3).

Found %: C 66.53; 66.78; H 11.20; 11.20

$C_{12}H_{24}O_3$. Calculated %: C 66.63; H 11.19

Preparation of the Acid (V)

A solution of 5.2 g of stannic chloride in 20 ml of benzene was added with stirring at 0° to a solution of 1.8 g of 2,2'-methylenedithiophene (I) and 3 g of the acid chloride of the monomethyl ester of succinic acid in 20 ml of dry benzene. The mixture was stirred at room temperature for four hours, and decomposition was then effected with dilute hydrochloric acid. The ester obtained was hydrolyzed when solvent was steam-distilled off. Prolonged extraction of the crude acid with water in a Soxhlet yielded 1.8 g (47.5%) of the acid (V), which melted at about 200°. After crystallization from 50% acetic acid and then from alcohol it melted with much darkening at 205-207°. The neutralization equivalent was found to be 191.1 (calculated value 190.2).

Found %: C 53.65; 53.64; H 4.18; 4.15; S 16.81; 16.71

$C_{17}H_{16}O_6S_2$. Calculated %: C 53.67; H 4.24; S 16.86

Preparation and Hydrogenolysis of the Acid (VI)

1. A mixture of 4.5 g of the acid (V), 7 ml of 100% hydrazine hydrate, and 50 ml of diethylene glycol was boiled for 15 minutes. Caustic potash (5 g) was added to the cooled solution, and the mixture was boiled for 90 minutes; water and excess of hydrazine hydrate were then distilled off. Boiling was continued for a further four hours at 180-200°, and the reaction mixture was then acidified, when 2.9 g (70%) of the acid (VI) separated. Crystallization, first from 50% acetic acid and then from 20% acetic acid, yielded 2.2 g of the acid, m.p. 106-108°. After recrystallization from water it melted at 119-119.7°. The neutralization equivalent was found to be 174.7 (calculated value 176.2).

Found %: C 57.58; 57.66; H 5.81; 5.80

$C_{17}H_{20}O_4S_2$. Calculated %: C 57.93 H 5.72

2. A mixture of 2 g of the acid (VI) in 20 ml of 10% sodium carbonate solution, 180 ml of water, and Raney nickel prepared as indicated above from 70 g of alloy was heated with stirring for about two hours at 90°. In the filtrate and in the alkaline solution obtained by washing the catalyst only traces of the required acid could be detected. The nickel was therefore dissolved in 120 ml of concentrated hydrochloric acid, and the solution was extracted four times with ether. Evaporation of the ether left 0.7 g of the acid (VII), m.p. 104-106°, raised by two crystallizations from ethyl acetate to 118-118.7°. For heptadecanedioic acid the literature [8] gives 117.5-118.6°. The neutralization equivalent was found to be 151.1 (calculated value 150.2).

Found %: C 68.04; 67.82; H 10.81; 10.61

$C_{17}H_{32}O_4$. Calculated %: C 67.96; H 10.74

LITERATURE CITED

[1] Ya. L. Goldfarb and M. S. Kondakova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, 1131* I. S. Korsakova, Thesis Moscow, 1953; Ya. L. Goldfarb and I. S. Korsakova, Proc. Acad. Sci. USSR 96, 293 (1954); Ya. L. Goldfarb and B. P. Fabrichny, Proc. Acad. Sci. USSR 100, 461 (1955).

[2] G. M. Badger, H. I. Rodda, W.H.F. Sasse, J. Chem. Soc. 1954, 4162.

[3] N. P. Buu-Hoi, M. Sy N. Dat Xuong, Comptes rend. 240, 442 (1955).

[4] Hyang-Minlon, J. Am. Chem. Soc. 68, 2487 (1946).

[5] Organic Syntheses 4, 349, Moscow, 1953.

[6] W. H. Lycan, R. Adams, J. Am. Chem. Soc. 51, 625 (1929).

[7] P. Chuit, J. Hausser, Helv. 12, 463 (1929).

[8] A. Kreuchunas, J. Am. Chem. Soc. 75, 3339 (1953).

Received March 22, 1955

N. D. Zelinsky Institute of Organic
Chemistry of the USSR Academy of Sciences

---

* See Consultants Bureau Translation, p. 993.

BLANK
PAGE

RELATION BETWEEN THE MOBILITIES OF IONS IN SOLUTION AND THEIR SELF-DIFFUSION COEFFICIENTS

O. Ya. Samoilov

According to firmly established concepts relating to the nature of the thermal movements of particles in liquids, and of ions in aqueous solutions in particular, the formation of a stream of ions in a solution under the action of an electric field results from the fact that the average number of activated jumps by ions in the direction of the field is greater than the number in the opposite direction [1]. Let φ be the work done by the field in moving an ion by a distance $\frac{\bar{l}}{2}$ in the direction of the field ($\bar{l}$ is the distance between adjacent equilibrium positions of ions in the structure of the solution – the mean length of the activated jumps of the ions). The work φ is done in moving the ion from its equilibrium position to the top of the potential barrier surrounding this position. Polissar [2] made the first evaluation of the value of φ for an aqueous solution of potassium chloride, and he showed that when the field was not too great $\varphi \ll kT$ (k is Boltzmann's constant, and T is absolute temperature). When this condition is applied, the excess of the number of jumps of ions in the direction of the field over the number in the reverse direction will be [1]

$$\Delta j = \frac{1}{6} \frac{f}{kT} j\bar{l},$$

(j is the average number of jumps made by each ion in one second, and f is the force acting on the ion in the electric field — we shall assume that the field gradient is 1 V/cm). The mean velocity of ions in the direction of the field will be

$$\bar{v} = \Delta j \bar{l} = \frac{1}{6} \frac{f}{kT} j\overline{l^2} \qquad (1)$$

The self-diffusion coefficient of the ion in solution is [1, 2]:

$$D = \frac{1}{6} j\overline{l^2} \qquad (2)$$

It will be seen from Equations 1 and 2 that, accurate within $\overline{l^2} - \bar{l}^2$, (square of the mean square fluctuation of the value of l)

$$\bar{v} = \frac{f}{kT} D \qquad (3)$$

and for the mobility of the ions $U = \bar{v}F$ (F being the faraday):

$$U = \frac{fF}{kT} D. \qquad (4)$$

Equation 4 is Nernst's equation, being obtained by him in 1888 in a treatment of the movement of ions in solutions regarded as the movement of spheres in a continuous viscous medium. The approximate character of Equation 4 should be noted. However, since the degree of short-range order in the arrangement of particles in water and in aqueous solutions of electrolytes is probably fairly high [3], the mean square fluctuation of l may be small.

In a number of cases the translationary movement of particles in liquids must be regarded as activated jumps of two kinds [4]: jumps of isolated particles and jumps of the "cells" as a whole. This approach is extremely useful in the study of the movement of ions in solutions. In the study of self-diffusion in electrolyte solutions the question arises of whether the ion makes the activated jumps without its solvation envelope, or with it. It is clear that jumps of both kinds can occur in solutions, so that it is necessary to take both sorts of jumps into account.* It is found, however, that Equation 4 still remains valid.

Activated jumps made by an ion in association with its solvation envelope must evidently be regarded as jumps by cells. In accordance with Equation 4 we then obtain the following expression for the self-diffusion coefficient of ions in solutions:

$$D = \frac{1}{6}\left(j_1\overline{l}_1^{\,2} + j_2\overline{l}_2^{\,2}\right). \qquad (5)$$

The subscripts 1 and 2 refer respectively to jumps by an isolated ion and jumps by a cell (an ion together with its solvation envelope).

Taking into account jumps of both kinds, we obtain for the mean velocity of the ion in the external electric field:

$$\overline{v} = \Delta j_1\overline{l}_1 + \Delta j_2\overline{l}_2. \qquad (6)$$

The force $\underline{f}$ exerted by the electric field on the ion is the same whether the jumps occur without the solvation envelope or with it, and the condition $\varphi \ll \underline{kT}$ [1, 2] is fulfilled for both kinds of jump. Hence

$$\Delta j_1 = \frac{1}{6}\,\frac{f}{kT}\,j_1\overline{l}_1 \quad \text{and} \quad \Delta j_2 = \frac{1}{6}\,\frac{f}{kT}\,j_2\overline{l}_2.$$

Substituting these values in Equation 6 we obtain

$$\overline{v} = \frac{1}{6}\,\frac{f}{kT}\left(j_1\overline{l}_1^{\,2} + j_2\overline{l}_2^{\,2}\right). \qquad (7)$$

Comparison of Equations 5 and 7 shows that, even when the jumps of the cells as a whole are taken into account, the relations in Equations 3 and 4 are observed approximately. As the structure of dilute aqueous electrolyte solutions is very similar to that of water [3], the values of $\overline{l}_1$ and $\overline{l}_2$ are not greatly different in such solutions (they may even be regarded as equal). Hence, the accuracy of Equation 4 is the same whether or not the jumps of cells are taken into account.

Received January 12, 1955

N. S. Kurnakov Institute of General and Inorganic
Chemistry of the USSR Academy of Sciences

---

* It is not assumed that the ion is firmly attached to any particular number of water molecules. The term "solvation envelope" refers to a definite number of constantly interchanging water molecules immediately surrounding an ion. The necessity for taking account of activated jumps made by an ion in association with such a solvation envelope is a consequence of the views that we have developed [4] on the mechanism of self-diffusion in liquids.

LITERATURE CITED

[1] K. Wirtz, Z. Naturforschung 3a, 672 (1948).

[2] Milton J. Polissar, J. Chem. Phys. 6, 833 (1938).

[3] O. Ya. Samoilov, J. Phys. Chem. 20, 1411 (1946); Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, No. 4, 627. *

[4] O. Ya. Samoilov, Proc. Acad. Sci. USSR 101, 125 (1955).

---

* See Consultants Bureau Translation, p. 585

BLANK
PAGE

RADIOCHEMICAL INVESTIGATION OF SPALLATION AND FISSION REACTION PRODUCTS RESULTING FROM THE BOMBARDMENT OF BISMUTH WITH 660-Mev PROTONS

A. N. Murin, B. K. Preobrazhensky and N. E. Titov

INTRODUCTION

A fairly detailed study has now been made of spallation reactions occurring as a result of the bombardment of light and medium-weight nuclei (e.g., Al [1], Fe [2], Cu [3, 4], As [5], Sb [6], Cs [7], Co [8], etc.) with high-speed particles. In all of these cases fission does not occur — at least not to a significant extent. When heavy elements are bombarded with high-speed particles, not only spallation reactions, but also fission reactions occur. The nature of these fission processes has been studied fairly thoroughly in an investigation [9] on the bombardment of bismuth with 190-Mev deuterons, but the products of the spallation reactions were not isolated. Spallation reactions (and also fission reactions) with 480-Mev protons were studied by us in collaboration with Nikitin [10], and also later by Bennett [11]: in the latter investigation only a few of the reaction products were studied and the absolute yields were not determined. In work on the bombardment of uranium with 380-Mev α-particles [12], not only fission products, but also some spallation products were isolated, but again the latter were not studied in detail.

In the present work we have investigated spallation and fission reactions occurring when bismuth is bombarded with 660-Mev protons, and we have discovered some of the laws governing the process. We have estimated the ratio of the reaction cross-sections for fission and for spallation, and we have also made comparisons with results obtained for the bombardment of bismuth with protons of lower energy (480 Mev) and with results obtained by Perfilov and Ostroumov's method of thick-layer plates [13]. All these considerations enable us to form a fairly complete picture of the process that is occurring and to reach interesting conclusions.

EXPERIMENTAL

Chemical Separation of Reaction Products

The target was either a plate of pure bismuth, 3-6 mm in thickness, or pure bismuth oxide powder wrapped in aluminum foil. After the bombardment the target was brought into solution, and small amounts (10-20 mg) of inert carriers for elements to be isolated were added to the solution. Isolation of the radioactive elements with their carriers was then carried out.

We outline below the procedures employed for the isolation of radioactive fractions of individual elements in a radiochemically pure form. Nearly all of the operations indicated were repeated many times.

Fe. Extraction with ether from 6 N HCl; separation of Tl and sulfides insoluble in acid; precipitation of $Fe(OH)_3$ with excess of ammonia.

Cu. Separation of hydroxides insoluble in ammonia (together with iron), separation of AgCl; precipitation of CuCNS from acid solution after reduction with SO_2.

Sr. Separation of sulfides insoluble in acid, and also $Fe(OH)_3$; separation of Ca with a mixture of alcohol and ether from the dry nitrates; separation of $BaCrO_4$; precipitation of $SrCO_3$ and $SrSO_4$.

Mo. Extraction with ether from 6 N HCl after oxidation; separation of $Fe(OH)_3$ with ammonia; precipitation with α-benzoinoxime from 3 N HNO_3, and then as MoS_3.

Ag. Precipitation of AgCl, dissolution in ammonia and separation of $Fe(OH)_3$; precipitation of Ag_2S in an ammoniacal medium; precipitation of AgCl.

Ba. Separation of sulfides insoluble in acid, and $Fe(OH)_3$ with ammonia; precipitation of $BaCO_3$, $BaCrO_4$.

Ce. Precipitation as CeF_3; precipitation as $Ce(IO_3)_4$ after oxidation with $KBrO_3$; separation of $Zr(IO_3)_4$ after reduction with hydrogen peroxide; precipitation of $Ce(OH)_3$ and $Ce_2(C_2O_4)_3$.

W. Precipitation of tungstic acid, dissolution in ammonia, and separation of $Fe(OH)_3$; separation of Ag_2S in ammoniacal medium; separation of MoS_3 in presence of tartaric acid; precipitation of tungstic acid.

Os. Distillation as OsO_4 from 2 N HNO_3; precipitation as sulfide.

Ir, Pt. Precipitation of chloroplatinate and chloroiridate by salting out with NH_4Cl after oxidation with aqua regia; repeated dissolution and salting out in a nonoxidative medium (to avoid precipitation of Pd); boiling with aqua regia to remove Os and Ru completely; separation of Ir by hydrolysis (boiling with $BaCO_3$); fractional precipitation of Ir and Pt as metals by means of formic acid.

Au. Extraction from 1.5 N HCl; precipitation with ammonia; precipitation of gold with hydroquinone; reprecipitation with SO_2.

Hg. Precipitation of HgS, washing with ammonium polysulfide; separation of other Group IV sulfides by dissolution in hot 2 N HNO_3; distillation of mercury at red heat; precipitation of HgS.

Tl. Extraction of $TlCl_3$ from 6 N HCl with ether after oxidation of Tl^+ to Tl^{+++}, precipitation with excess of ammonia; separation of gold with hydroquinone; precipitation of TlI after reduction with SO_2.

Pb. Precipitation of PbS; precipitation of $PbSO_4$, dissolution in ammonium acetate, and precipitation of $PbCrO_4$.

Bi. Precipitation of Bi_2S_3, washing with ammonium polysulfide. Separation of AgCl; separation of $PbSO_4$, precipitation of BiOCl.

Po. Karraker and Templeton's method of purifying Po [14] was adopted. Experiments showed that in the present case no other comparatively long-lived α-emitters, apart from Po were formed in appreciable amount. For this reason, Po preparations obtained from the original solution by separation on silver foil or simply by evaporation of a known fraction of the solution showed the same α-activity as purified preparations.

Counting Procedure and Determination of Yields

The preparations prepared for measurement consisted of precipitates, about 10-15 mg in weight, filtered off on flat round filters, 2 cm in diameter, placed on standard aluminum dishes having low sloping sides and perforated bottoms. The dishes were prepared from aluminum foil, 0.5 mm in thickness. The activities of the preparations isolated were measured by suitable counting devices, operated for the necessary periods of time, and yields were calculated from the results obtained.

In order to convert relative yields into the absolute cross section for the formation of the given isotope, monitor aluminum foils were bombarded simultaneously with the target, and in these Na^{24} was formed by the reaction Al^{27} (p; 3p, n). The cross section for this reaction was taken to be 11 millibarns. The isotope Sr^{89} was generally taken as the standard for comparison (it was isolated in every bombardment), and the cross section for its formation was determined from the yield of Na^{24} from Al.

Measurements on isotopes that undergo β-decay (mainly fission products — apart from the heaviest fragments, that undergo K-capture and emit positrons) were carried out with a standard end-on counter having a thin mica window.

When necessary, the identification of the isotopes was confirmed by determining the energy of the β-radiation by the absorption method or with a rough β-spectrometer. Measurements of α-activity were made with the aid of an ionization chamber connected to a linear amplifier.

The most difficult problem was the determination of the yields of isotopes undergoing electron capture with subsequent emission of X-rays and γ-quanta. Such isotopes form most of the spallation products of the reaction studied. In this case, whatever the method of measurement may be, for the exact determination of the yield it is necessary to know the precise way in which the given isotope disintegrates and to have data concerning the energy and number of γ-quanta per act of disintegration and the corresponding conversion coefficients, and also concerning the ratio of K- to L-capture; it is, moreover, necessary to take account of fluorescence yield and the presence of Auger electrons and of various X-radiation attributable to them. In such a case it is expedient to use various filters in order to isolate the desired form of radiation, for which the intensity (per disintegration event) and counting efficiency in the counting device employed are known. We used two methods of measurement, which could be checked against each other. Counting efficiencies for quanta of electromagnetic radiation varying in hardness have been determined by other authors for the two counting devices that we used [14, 15].

First, we used a standard end-on counter provided with beryllium, aluminum, and lead filters. Second, we used a B-1 cylindrical counter (diameter 10 mm, thickness of aluminum wall 0.1 mm) having an aluminum jacket 3 mm in thickness. Electrons and soft X-rays (L_x, M_x, etc.) were absorbed in this jacket, and only K-rays and γ-quanta were counted in the counter. For this counter we determined the counting efficiency — which included also the geometric factor — for the γ-radiation of a Co^{60} preparation (mean energy of γ-quanta 1.25 Mev) having a known number of disintegrations per second. The relative efficiencies of the counter for γ-quanta of other energies were determined from the curve given in the paper [15] for the dependence of efficiency on energy for a counter with an optimum aluminum cathode. All preparations were measured with these two counting devices, and in the majority of cases the results were in satisfactory agreement.

The errors in our calculated values for the production cross sections for the various reaction products are made up of individual errors in the determination of individual factors; some of these are small, but others may be considerable and, moreover, difficult to calculate. However, the agreement found between the values of yields determined by different methods shows that the precautions taken were probably adequate, enabling large errors to be avoided.

DISCUSSION OF RESULTS

The reaction products isolated and their measured formation cross sections are given in the table and in Fig. 1. With rare exceptions the fission and spallation products formed were found to be radioactive nuclei converted by a definite chain of disintegrations into stable nuclides. It was, therefore, considered to be most expedient to isolate the last members of the active chains, which are generally comparatively long-lived (formed usually from isobars of considerably shorter life) and which pass finally into stable nuclei. The yields of these last members of the chains generally include almost the whole of the yield of all isotopes with the given mass number.

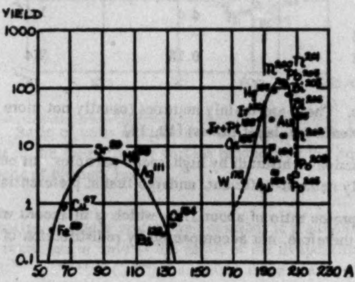


Fig. 1. Dependence of the yields (in millibarns) of fission and spallation products on the mass numbers of the nuclei formed.

However, we must also take into account the possibility that the last member of the chain may have a comparatively short half-life and may exist at the moment of its isolation as a result of its formation from a predecessor of longer life, e.g.:

$$Pt^{188} \xrightarrow[T\,=\,10.3\text{ days}]{} Ir^{188} \xrightarrow[T\,=\,42\text{ hours}]{} Os^{188}\text{ (stable)}^{*}$$

In such cases repeated separations of daughter and mother elements were made at different times after the end of bombardment, and this permitted, in particular, the determination of their independent yields. Items in the table that are enclosed in rectangles refer to isotopes whose nuclei are "screened" by stable isobars and are, therefore, obtained in independent yield, so that the yield does not refer to all products of the given mass number. In Fig. 1, points representing these yields are marked by black squares.

The main conclusion that can be derived directly from the experimental results is that the ratio of the cross sections of Bi for fission and spallation reactions is 7% for 660-Mev protons; in accordance with data that we have checked it is 5% for 480-Mev protons.

---

[*] The existence of the isotope Pt^{188}, which we discovered in earlier work, has recently been confirmed [17].

TABLE 1

Summary Table of the Measured Cross Sections for the Products

Isotope	σ_{mb} 660 Mev		σ (660) mean (weighted)	σ (480) (cylindrical counter [10])	σ (660)/σ(480) cylindrical counter
	end-on counter	cylindrical counter			
Po 208	–	3.3 (α)	3.3	3.1	–
Po 206	–	3.0 (α)	3.0	2.6	–
Bi 206	90	61	75	71	0.85
Bi 205	83	73	78	77	0.9
Pb 203	132	90	110	100	0.9
$\boxed{\text{Tl 202}}$	$\boxed{10}$	$\boxed{20}$	$\boxed{15}$	$\boxed{12.3}$	$\boxed{1.6}$
Tl 201	110	140	125	129	1.1
Tl 200	142	140	140	130	1.1
Hg 197	82	86	87	86	1.0
$\boxed{\text{Au 196}}$	$\boxed{2}$	$\boxed{5}$	$\boxed{3.5}$	$\boxed{3.0}$	$\boxed{1.6}$
Au 195	22	28	28	26	1.1
$\boxed{\text{Au 194}}$	$\boxed{8}$	$\boxed{12}$	$\boxed{10}$	$\boxed{5.6}$	$\boxed{2.1}$
Ir 190	47	–	47	–	–
Ir 188	2.1	–	2.1	–	–
Pt 188	27	–	27	–	–
Os 185	15	14	15	–	–
W 178	2.5	1.8	2.5	0.78	2.3
Ce 134	–	0.42	0.42	0.11	3.8
Ba 128	–	0.3	0.3	0.2	1.5
Ag 111	3.7	–	3.7	3.1	1.2
Mo 99	5.4	–	5.4	4.4	1.23
Sr 89	6.4	6.4	6.4	4.4	1.45
Cu 67	0.86	–	0.86	–	–
Fe 59	–	0.36	0.36	0.15	2.4

Before fission occurs, 15-16 nucleons leave the nucleus. These are mainly neutrons (usually not more than one or two protons, this being confirmed also by experiments on thick-layer plates) [12, 16].

This behavior confirms the emission character of the fission of bismuth by high-speed particles. In our case it appears that Po, Bi, Pb and Tl nuclei, which are highly neutron-deficient, undergo fission preferentially.

The fission fragments are characterized by a neutron-proton ratio of about 1.35, which is in accord with the results of other authors [9]. Fission by rapid particles is, therefore, not accompanied by redistribution of charges in the fragments formed.

It was found that in the spallation of the bismuth nucleus by 660-Mev protons, on the average 2 protons and 8 neutrons are ejected. When the interpolated yields of nonisolated products are taken into account, approximately the same values are obtained. We must point out that this number of protons may be too high, and the number of neutrons correspondingly too low (apparently not more than by unity), owing to the fact that we separated not only the immediate reaction products, but also their daughter products. Unlike the spallation products of light and medium-weight nuclei, those obtained from bismuth were mainly neutron-deficient (compared with stable nuclei).

The formation of stable nuclei is found to be very unlikely (this view is supported also by the low yields of screened isotopes). However, in those cases in which an element has many stable isotopes and the stability region extends to fairly light isotopes of this element (as in the case of Hg and Pt), these light stable isotopes may be obtained directly to an appreciable extent. For certain mass numbers, therefore, it was not possible to determine the yield experimentally, although it could be estimated approximately by interpolation on the curve for the yields.

Fig. 2 shows that the yields of nuclei far-removed from the target nucleus with respect to A and Z increase with increase in the energy of the bombarding particles. At the same time, however, there is also a relative increase in the yields of "screened" nuclei (see table), i.e., nuclei corresponding to enhanced reduction in the charge of the target nucleus (greater ΔZ) for a given fall in the mass number (ΔA).

It must be remembered that the formation of a given nucleus is determined by the total numbers of protons and neutrons knocked out and evaporated in the spallation reaction.* Thus,

$$\Delta Z = p_k + p_e$$

$$\Delta (A-Z) = n_k + n_e$$

($\underline{p}$ is the number of protons, $\underline{n}$ the number of neutrons, and $\underline{k}$ and $\underline{e}$ indicated "knocked out" and "evaporated", respectively). For a given value of ΔA the mean value of $\overline{\Delta Z}$ will be the greater, the greater the ratio of the number of particles knocked out to the number evaporated, since the ratio $\underline{p_k}/\underline{n_k}$ is, in general, greater than $\underline{p_e}/\underline{n_e}$ (neutrons always predominate greatly in the evaporation component). Hence, as the energy of the particles increases, ΔZ (for given ΔA) increases, and the curve for the distribution of the yields of products having given values of A is displaced in the direction of products less deficient in neutrons.

The fission of nuclei formed from bismuth nuclei as a result of spallation has an emission character [9]; in other words, the neutron breadth Γ_n is greater than the fission breadth Γ_f for nuclei having an excitation energy of $\underline{u} \gg 10$ Mev.

Hence, the character of the fission process (and, therefore, also the yield distribution curve for the products) for a nucleus having given values of Z and A−Z does not depend on the energy of the bombarding particle (all highly excited states are "removed" by prior evaporation of nucleons). With increase in the energy of the bombarding particle, the relative number of light nuclei undergoing fission increases and the fission yield curve (see Fig. 2) becomes broader and is displaced to lower values of A and Z. However, as can be seen from Curve 1 in Fig. 2, with increase in the energy of the bombarding particles there is an increase also in the relative yield of heavy fission products; this can be explained either by the asymmetric character of the fission of neutron-deficient nuclei, or less probably, by a supplementary yield of heavy fragments resulting from the "intrusion" of spallation products into the region of fission products. The formation of these isotopes as a result of the ejection and evaporation of single protons and neutrons is practically impossible. As can be shown from simple energy considerations, it can occur only as the result of the evaporation of a large number of α-particles [e.g., a reaction of the form $Bi^{209}(p^{12\alpha;\,24n})Ce^{134}$], i.e., when there is a very considerable, and therefore very unlikely, departure of the number of α-particles from the mean. It is possible also that this isotope may be formed as a result of the ejection of larger fragments, which is to a certain extent a variant of the phenomenon of asymmetrical fission. A final solution of the problem must await further experiments.

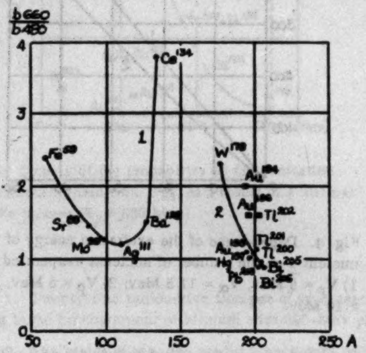


Fig. 2. Ratio of cross sections for 660-Mev and 480-Mev protons in the formation of various products by the bombardment of bismuth nuclei.

The spallation products that we observed were formed as the result of a nuclear cascade process which leads to the ejection of several nucleons from the bismuth nucleus (and, if proton capture occurred, from a polonium nucleus) with subsequent emission of further nucleons by evaporation from the excited nucleus. For a given excitation energy $\underline{u}$ of the nucleus, the total number of evaporated nucleons can be calculated by an application of the simplest variant of the theory with the aid of the equations:

$$\frac{du}{dA} = \frac{\Gamma_p(\epsilon_p + 2T + V_p) + \Gamma_n(\epsilon_n + 2T) + \Gamma_\alpha(\epsilon_\alpha + 2T + V_\alpha)}{\Gamma_p + \Gamma_n + 4\Gamma_\alpha};$$

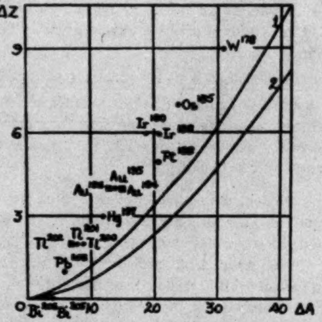
$$\frac{\Gamma_p}{\Gamma_n} = \left(1 + \frac{V_p}{T}\right) e^{-\frac{V_p}{T}} \frac{Z}{A-Z};$$

---

* The evaporation of α-particles (which we shall take into account in our further considerations) does not affect the general sense of these discussions.

$$\frac{\Gamma_\alpha}{\Gamma_p} \approx 0.5.$$

(A is the number of nucleons in the nucleus; T is the temperature of the nucleus ($\underline{u} \approx 0.1\ AT^2$); ϵ_x is the binding energy of the particles in the nucleus ($\epsilon_p = \epsilon_n \approx 8$ Mev; $\epsilon_\alpha = -3$ Mev); V_α is the coulomb barrier, V_p being the barrier for protons; Γ_p, Γ_n, and Γ_α are the respective breadths, proportional to the probabilities for the escape of the particles from the excited nucleus). The ratio Γ_α/Γ_p was taken as 0.5 (data from the paper [5]).



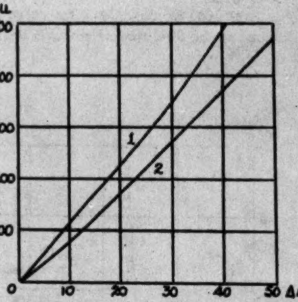


Fig. 3. Dependence of the loss of charge ΔZ by the target nucleus Bi^{209}_{83} on the number (ΔA) of nucleons knocked out and evaporated: 1) $V_p = 5$ Mev, $V_\alpha = 10$ Mev; 2) $V_p = 8$ Mev, $V_\alpha = 17.5$ Mev.

Fig. 4. Dependence of the excitation energy of the nucleus $\underline{u}$ on the number of nucleons evaporated (ΔA): 1) $V_p = 8$ Mev, $V_\alpha = 17.5$ Mev; 2) $V_p = 5$ Mev, $V_\alpha = 10$ Mev.

It is difficult to estimate the height of the effective barrier (V_p or V_α): for strongly excited nuclei it is considerably less than for the nucleus in the ground state [5]. For comparison purposes we made the calculations for two values of each parameter: $V_p = 8$ Mev, $V_\alpha = 17.5$ Mev and $V_p = 5$ Mev, $V_\alpha = 10$ Mev (the second case is unlikely to represent actual conditions).

Fig. 3 presents our calculated curves for the dependence of the loss of charge ΔZ (ΔZ = 83−Z of the nucleus formed) on the change in mass number (ΔA = 209−A of the nucleus formed). It is clear that ΔA is simply the total number of nucleons evaporated. The nuclei that we observed (more accurately, the corresponding experimental points) are represented by circles, against which the symbols of the corresponding isotopes are placed.

An examination of the curves in Fig. 4 shows that the value of $\underline{u}$ (and still more $\underline{dA}/\underline{du}$, see below), expressed as a function of ΔA, is not greatly dependent on which variant is chosen for the values of V_p and V_α.

If we assume that in all cases the Bi nucleus lost five nucleons as a result of the nuclear cascade process before the evaporation process began,* then it is possible to construct — to a very rough approximation, of course — a curve for the distribution of the probability of excitation of the nucleus to a given energy $\underline{u}$ [$W'(\underline{u})$ is approximately equal to $\underline{d}\sigma_{total}/\underline{du}$, in which σ_{total} is the total cross section for the nonelastic interaction of a proton with a bismuth nucleus]. It should be noted that

$$W(u)\,dA = W(u)\frac{dA}{du}\,du = W'(u)\,du.$$

---

* For 700-Mev protons and a bombarded nucleus having a mass number of about 100, the number of nucleons knocked out (excluding the bombarding proton) is approximately 3 [18]. The number of nucleons knocked out increases comparatively slowly with increase in A. If we assume that it is proportional to $A^{2/3}$, we obtain for a Bi nucleus bombarded with such protons the value of 5-6 ejected nucleons.

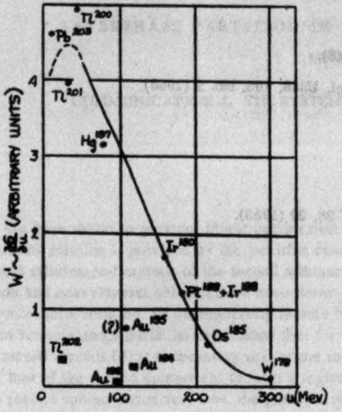


Fig. 5. Density of the probability of the excitation of a nucleus formed from Bi_{83}^{209} as a result of a nuclear cascade process (E_p = 660 Mev).

In these equations W(u) is the density of the probability, calculated per unit interval of mass number; W'(u) is the probability per unit interval of excitation energy. The values of W'(u) are found by comparison of the yield curves in Fig. 1 and the lower curve in Fig. 4. The last curve can also yield the corresponding values of the derivative dA/du.

The results of such transformations are shown in Fig. 5. The mean excitation energy is here found to be about 90 Mev. Choice of the second variant for the values of the parameters V_p and V_α leads us to a lower and probably less reliable value of u (about 70 Mev). The indicated value of u must be regarded as only a comparatively crude approximation, probably somewhat less than the true value of the mean excitation energy, although it agrees excellently with calculated results [16]. It is probable that in actual fact, the formation of nuclei far-removed in Z and A from the target nucleus occurs after the ejection of fewer particles than we have assumed in our calculation (about 5).

In conclusion, it is our pleasant duty to express our deep gratitude to M. G. Meshcheryakov and the operating staff of the synchrocyclotron of the Institute of Nuclear Problems of the USSR Academy of Sciences for help in the performance of the experiments.

SUMMARY

1. Twenty-four radioactive isotopes of seventeen elements were isolated and identified in the products arising in the bombardment of bismuth with 660-Mev protons.

2. The yields of reaction products were determined. The ratio of cross sections for fission and spallation reactions was found to be about 0.07.

3. The fission reaction is preceded by the ejection, on the average, of 15-16 nucleons. In the spallation reaction 2 protons and 8 neutrons are ejected, on the average.

4. As the energy of the bombarding protons increases there is a displacement of the yields into the stability region and also, probably, an increase inthe asymmetry of the fission of strongly excited nuclei. The results permit an estimation of the mean excitation energy of the nuclei formed as a result of the nuclear cascade process, the value found being about 90 Mev.

V. G. Khlopin Radium Institute of the
USSR Academy of Sciences

Received April 14, 1955

LITERATURE CITED

[1] L. Marquez, Phys. Rev., 86, 405 (1952).

[2] G. Rudstam and others, Phys. Rev., 87, 358 (1952).

[3] R. Batzel, D. Miller, G. Seaborg, Phys. Rev., 84, 671 (1951).

[4] L. Marquez, Phys. Rev., 88, 225 (1952).

[5] H. Hopkins, Phys. Rev., 77, 717 (1950).

[6] M. Lindner, I. Perlman, Phys. Rev., 78, 499 (1950).

[7] R. Fink, E. Wiig, Phys. Rev., 94, 1357 (1954).

[8] E. Belmont, I. Miller, Phys. Rev., 96, 1554 (1954).

[9] R. Goeckerman, I. Perlman, Phys. Rev., 76, 628 (1949).

[10] B. A. Nikitin, A. N. Murin and B. K. Preobrazhensky, in the press (submitted 1953).

[11] W. Bennett, Phys. Rev., 94, 997 (1954).

[12] P. O'Connor, G. Seaborg, Phys. Rev., 74, 1189 (1948).

[13] N. A. Perfilov and V. I. Ostroumov, Proc. Acad. Sci. USSR, 103, No. 2 (1955).

[14] Karraker, Templeton, Phys. Rev., 81, 510 (1951).

[15] G. Wilkinson, Phys. Rev., 80, 495 (1950).

[16] H. Bradt, Helv. Phys. Acta., 19, 77 (1946).

[17] McManus, Sharp, Gelleman, Bull. Am. Phys. Soc., 28, 20 (1953).

[18] R. Naumann, Phys. Rev., 96, 90 (1954).

INTERPHASE PARTITION IN SYSTEMS CONTAINING ANOMALOUS MIXED CRYSTALS

COMMUNICATION 4. THE SYSTEMS $NH_4Cl-CuCl_2-H_2O$ AND $NH_4Cl-CrCl_3-H_2O$

E. M. Ioffe

We have shown in previous investigations that a good criterion for systems consisting of anomalous mixed crystals and solution is provided by the partition coefficient for the distribution of a microcomponent between the saturated solution and crystals of the second substance. Applying this criterion to systems consisting of ammonium chloride and heavy-metal chlorides, we have shown [1] that in the case of the system $NH_4Cl-FeCl_3-H_2O$ we have a colloidal solid solution, its distinguishing feature being the existence of a lower limit for its formation. The work of Khlopin and Nikitin has established that for the formation of mixed crystals of a new type [2] and of anomalous mixed crystals [3] it is necessary that at the surface of the growing crystal there should be a sufficient number of ions of the second component to form a region of its own crystal lattice. When, however, the concentration of the second component is very low, the probability of a number of simple or complex ions of the second component being found in close array is very slight, and mixed crystals cannot be formed. This implies that in such systems there will be a lower limit for mixed-crystal formation. In the case of true mixed crystals, in which replacement occurs ion for ion or atom for atom, a lower limit for mixed-crystal formation was never observed.

For the system $NH_4Cl-FeCl_3-H_2O$ we showed that when the concentration of iron in the solution falls below a certain value, the partition coefficient for the distribution of iron begins to fall, tending to zero. This proves the existence of a lower limit for mixed-crystal formation in this system containing iron. Before we can claim that the existence of a lower formation limit is a criterion for the differentiation of true from anomalous mixed crystals, it is essential to study a number of typical systems. Study of a system consisting of ammonium chloride and the chloride of a bivalent metal, namely $NH_4Cl-MhCl_2-H_2O$, showed its great difference from the analogous system containing iron. Whereas in the system $NH_3Cl-FeCl_3-H_2O$ the partition coefficient began to fall at an iron concentration of about 10^{-2} mole/l for the manganese system it remains constant over a wide range of concentrations and down to 10^{-6} mole per liter. Moreover, the actual values of the partition coefficients differ greatly, the value for manganese (0.76) being almost thirty times as great as that for iron (0.026 at its maximum).

The object of the present work was the verification of the conclusions that we had reached from partition studies on the systems $NH_4Cl-FeCl_3-H_2O$ and $NH_3Cl-MnCl_2-H_2O$ through the investigation of analogous systems.

EXPERIMENTAL

As an analog of the manganese system we selected $NH_4Cl-CuCl_2-H_2O$ because the ionic radius of bivalent copper is very close to that of bivalent manganese and the double salt $2NH_4Cl_2 \cdot MnCl_2 \cdot 2H_2O$ corresponds in composition to the double salt $2NH_4Cl \cdot CuCl_2 \cdot 2H_2O$.

We made use of the procedure developed by Khlopin [4] and his students for the study of the partition of a microcomponent between solid and liquid phases. There are three ways in which equilibrium may be attained. First, "from below": equilibrium is attained by recrystallization of crystals of the macrocomponent in its saturated solution containing the microcomponent. Second, the mixed crystals may be recrystallized in a saturated solution of the pure macrocomponent. Third, equilibrium may be attained by crystallization from supersaturated solutions with rapid stirring. All that has been written about the methods of attaining equilibrium in the case of true mixed crystals applies also, as our investigations have shown [5], to anomalous mixed crystals. In the present work we used the third method of attaining equilibrium.

One of the objects of the present investigation was, therefore, to determine whether or not a lower limit for mixed-crystal formation exists in the system $NH_4Cl-CuCl_2-H_2O$. We sought for this limit by determining the partition coefficient for various concentrations of microcomponent in the solution. The partition coefficient D is most conveniently expressed as follows:

$$\frac{x}{y} = D\,\frac{100-x}{100-y}$$

(x and y are the amounts of micro- and macro-components passing into the crystals, expressed as percentages of the total amounts in the system). The system was studied at 0°. Ammonium chloride that had been recrystallized three times was used.

The experiments were generally carried out as follows: the required amount of ammonium chloride crystals was weighed into a glass test tube, about 75 ml in capacity, and to this was added 30 ml of the original solution, which consisted of a solution of ammonium chloride saturated at 0° and containing a definite amount of cupric chloride as microcomponent. The test tube was closed with a ground stopper and heated in hot water until the solid phase had dissolved completely, when it was transferred to a thermostat containing melting ice. The solution was allowed to attain the temperature of the thermostat and was then stirred vigorously with a mechanically driven screw-shaped glass stirrer for four hours. Stirring was then discontinued and the stirrer removed. The crystals were removed from the mother liquor and washed with a solution of ammonium chloride which had been saturated at 0° and which was cooled to 0° before use.

TABLE 1

Amt. of Cu (g) per ml of original solution	Cu concentration (moles per liter)	Amt. of NH_4Cl precipitated (%)	Amt. of Cu in crystals (%)	D (according to the crystals)	D (according to the solution)	Method of determining copper
0.00222	$3.5 \cdot 10^{-2}$	30.0	21.2	0.62	–	Colorimetric
0.00222	$3.5 \cdot 10^{-2}$	30.0	20.7	0.61	–	"
0.00044	$7.0 \cdot 10^{-3}$	23.0	13.7	0.53	–	"
0.00044	$7.0 \cdot 10^{-3}$	20.0	12.7	0.56	0.58	"
0.00044	$7.0 \cdot 10^{-3}$	30.0	16.6	0.46	0.43	"
0.00044	$7.0 \cdot 10^{-3}$	30.0	16.2	0.45	–	"
0.00022	$3.5 \cdot 10^{-3}$	30.0	15.1	0.47	0.49	"
0.0000045	$7.0 \cdot 10^{-5}$	30.0	20.4	0.59	–	Colorimetric with preliminary precipitation with hydrogen sulfide
0.0000045	$7.0 \cdot 10^{-5}$	30.0	19.8	0.58	–	
$1.7 \cdot 10^{-5}$	$2.7 \cdot 10^{-4}$	30.0	16.7	–	0.47	Experiments with radioactive copper
$1.3 \cdot 10^{-8}$	$2.1 \cdot 10^{-7}$	30.0	18.8	0.54	–	
				Mean 0.53	Mean 0.49	

We followed the partition of the microcomponent between the liquid and solid phases by determining the copper contents of the original solution and the crystals, and sometimes also of the solution after the experiment. For copper concentrations in the range $3.5 \cdot 10^{-2}$ to $3.5 \cdot 10^{-3}$ mole per liter we determined copper colorimetrically with the aid of the blue color resulting from the formation of tetrachlorocuprate.

So that we could reduce the concentration of copper in the original solution and still obtain reliable results, we took a liter or more of the solution for each experiment instead of the usual 25-30 ml. In this way we succeeded in determining partition coefficients at a copper concentration of $7.0 \cdot 10^{-5}$ mole per liter in the original solution. In these experiments we first precipitated the copper with hydrogen sulfide in an acid medium. The calcined precipitate was dissolved in a few drops of hydrochloric acid, the solution was diluted with distilled water and neutralized, and colorimetric analysis was carried out in the usual way. The colorimetric determinations were accurate within 3-4%.

In order that the concentration of copper in the original solution might be reduced still further we went over to radiometric methods of analysis. For this purpose we used one of the radioactive isotopes of copper, namely Cu^{64}, which has a half-life of 12.8 hours. Measurements were carried out on the β-emission with a Type B apparatus fitted with a B_1 tube. The results obtained are shown in Table 1, in which D is the partition coefficient

The results show that for copper concentrations in the original solution ranging from 10^{-2} to 10^{-7} mole per liter the numerical value of the partition coefficient remains constant, being on the average 0.53 according to the crystals and 0.49 according to the solution.

As an analog of the system $NH_4Cl-FeCl_3-H_2O$ we selected the system $NH_4Cl-CrCl_3-H_2O$. Partition in this system was studied by the same methods as those used for the copper system, i.e., equilibrium was attained by crystallization from supersaturated solutions with rapid stirring. The system was studied at 0°.

The very first experiments showed that the coefficient for the partition of chromium between solid and liquid phases is extremely small in this system and it is necessary to use a radioactive indicator even with fairly high concentrations of chromium in the original solution. For this purpose we used one of the radioactive isotopes of chromium, namely Cr^{51}, which has a half-life of 26.5 days. Measurements were carried out on the β-emission with a Type B apparatus fitted with a B_1 tube. The original solutions were saturated with ammonium chloride at 0° and contained various amounts of chromic chloride as microcomponent.

The partition of chromium between liquid and solid phases was followed by analysis of the crystals only, and this was carried out as follows: the crystals were carefully dried in a silica beaker on a sand bath, treated with strong nitric acid, and left on the bath until removal of ammonium chloride was complete. The residue in the beaker was carefully dissolved in water, and the solution, which contained chromic chloride, was transferred a drop at a time to an aluminum dish, where it was evaporated with the aid of an infrared lamp. The activity of the crystals was measured with a β-ray counter. The activity of the original solution was determined in the same way.

The concentration of chromium in the original solution was determined gravimetrically by precipitation as hydroxide, calcination, and weighing as Cr_2O_3. The results are given in Table 2.

TABLE 2

Amt. of Cr (g) per ml of original solution	Cr concentration (moles per liter)	Amount of		D	Activity taken for experiment (impulses)	Activity in the crystals (impulses)
		NH_4Cl in crystals (%)	Cr in crystals (%)			
0.0291	$5.6 \cdot 10^{-1}$	30	0.11	0.0026	473,500	537
0.0291	$5.6 \cdot 10^{-1}$	30	0.08	0.0020	470,000	360
0.0204	$4.0 \cdot 10^{-1}$	30	0.10	0.0023	159,600	160
0.0151	$2.9 \cdot 10^{-1}$	30	0.12	0.0028	77,500	96
0.0151	$2.9 \cdot 10^{-1}$	30	0.09	0.0021	75,000	66
0.0135	$2.6 \cdot 10^{-1}$	30	0.08	0.0020	168,850	128
0.0135	$2.6 \cdot 10^{-1}$	30	0.09	0.0021	177,100	162
0.0115	$2.2 \cdot 10^{-1}$	30	0.11	0.0026	601,250	630
0.0115	$2.2 \cdot 10^{-1}$	30	0.10	0.0023	300,625	296
			Mean	0.0023		
0.0025	$4.8 \cdot 10^{-2}$	30	0.04	0.0010	73,650	27
0.0025	$4.8 \cdot 10^{-2}$	30	0.05	0.0012	73,620	38
0.0025	$4.8 \cdot 10^{-2}$	30	0.06	0.0014	69,225	40
0.0024	$4.6 \cdot 10^{-2}$	30	0.04	0.0010	51,450	23
0.0024	$4.6 \cdot 10^{-2}$	30	0.05	0.0011	51,450	29
			Mean	0.0011		
0.00044	$8.4 \cdot 10^{-3}$	30	Mixed crystals are not formed		26,875 26,875	2 3

The first series of experiments was carried out on solutions containing from 0.0291 to 0.0115 g of chromium per ml of solution. Over this range of concentrations the partition coefficient D remains constant in spite of a 2.5-fold reduction in the chromium content of the solution; its average value is 0.0023. In the second series of experiments the chromium content of the original solutions was 0.0025 g/ml, i.e., was further reduced in the ration 1:4.6. Table 2 shows that the partition coefficient is reduced to about one-half of its value in the previous series of experiments, i.e., to 0.0011, on the average. The last series of experiments was carried out on an original solution containing 0.0044 g of chromium per ml of solution. In these experiments all of the chromium remained in the solution, whereas 30% of the ammonium chloride taken passed into the precipitate. Hence, when the chromium concentration is reduced from 0.0291 to 0.00044 g/ml, the partition coefficient falls from its maximum value to zero, so that in this system there is a lower limit for the formation of mixed crystals.

Work with this system is greatly complicated as a result of the very low value of the partition coefficient, and reliable results can be obtained only by using preparations of very high specific activity. In order to compare the behaviors of all four systems, consisting of ammonium chloride with the chlorides of tervalent iron and chromium and bivalent manganese and copper, we shall represent the results graphically, taking as abscissas the negative logarithms of the molar concentrations of the microcomponent in the solution (C_M), and as ordinates - partition coefficients D expressed as percentages of their maximum values in the various systems. When the results are represented in this way, a clear indication is given of the dependence of the partition coefficient of the microcomponent on its concentration in the solution, and curves that are fully comparable with one another are obtained in spite of the fact that the values of the partition coefficients differ very greatly among themselves...

TABLE 3

Concentration of Fe, etc. (moles per liter)	C_M	D (mean)	D (% of maximum)	D maximum (mean)
		The System $NH_4Cl-FeCl_3-H_2O$		
0.27	0.57	0.026	94.6	0.0275
0.055	1.26	0.029	105.5	
0.017	1.77	0.015	54.6	
0.0059	2.23	0.005	18.2	
		The System $NH_4Cl-CrCl_3-H_2O$		
$5.6 \cdot 10^{-1}$	0.25	0.0023	100.0	0.0023
$2.7 \cdot 10^{-1}$	0.57	0.0023	100.0	
$2.2 \cdot 10^{-1}$	0.66	0.0024	100.5	
$4.8 \cdot 10^{-2}$	1.32	0.0011	48.0	
		The System $NH_4Cl-MnCl_2-H_2O$		
$4.0 \cdot 10^{-3}$	2.40	0.73	92.3	0.80
$8.0 \cdot 10^{-4}$	3.10	0.76	95.0	
$3.4 \cdot 10^{-4}$	3.47	0.78	97.5	
$6.6 \cdot 10^{-5}$	4.18	0.87	108.7	
$4 \cdot 10^{-5}$	4.40	0.75	93.8	
$4 \cdot 10^{-6}$	5.40	0.89	111.3	
		The System $NH_4Cl-CuCl_2-H_2O$		
$3.5 \cdot 10^{-2}$	1.45	0.61	115.0	0.53
$7 \cdot 10^{-3}$	2.46	0.50	94.3	
$2.7 \cdot 10^{-4}$	3.6	0.47	97.9	
$7.0 \cdot 10^{-5}$	4.15	0.58	109.4	
$2.3 \cdot 10^{-7}$	6.7	0.54	101.9	

Curves representing the dependence of the partition coefficient of the microcomponent on its concentration in the solution are shown in Fig. 1.

Curve 1, which is for the iron system, is at first parallel to the axis of abscissas, which indicates that in spite of a reduction in the iron content of the solution the partition coefficient remains constant. However, at a certain concentration the partition coefficient begins to fall, so that the curve proceeds at an angle to the axis of abscissas. Curve 2, which shows the dependence of the partition coefficient of chromium on its concentration in the solution, proceeds like the iron curve, remaining in the first place parallel to the axis of abscissas in spite of a reduction in concentration to less than one-half of the original value. With further reduction of the chromium content of the original solution, the partition coefficient begins to fall sharply, so that the curve proceeds at an angle to the axis of abscissas. The curve showing the dependence of the partition coefficients of bivalent manganese and copper on concentration is quite different in character from the curves for tervalent-metal chlorides which we have just considered: whereas in the iron and chromium systems the partition coefficients begin to fall when the concentration of the microcomponent in the solution is of the order of 10^{-2} mole per liter, in the manganese system over a concentration range of approximately 10^{-3} to 10^{-6} and in the copper system from 10^{-2} to 10^{-7} mole per liter, the partition coefficient remains constant. Fig. 1 shows that the curve for the manganese and copper systems is a straight line parallel to the axis of abscissas.

Comparing the partition behavior in the systems $NH_4Cl-MnCl_2-H_2O$ and $NH_4Cl-CuCl_2-H_2O$, we see that they behave in completely analogous ways. If in these systems there is a lower limit for the formation of mixed crystals, then it lies below the range that we have studied.

Most authors consider that the guest component in the manganese system is the complex anion $(MnCl_4 \cdot 2H_2O)^{=}$[6]. It is probable that in the copper system the guest component is the complex anion $(CuCl_4 \cdot 2H_2O)^{=}$. We consider that the views of Greenberg and Walden [7] are sound and are supported by reliable experimental data. These authors studied the structure of the double salt $2NH_4Cl \cdot MnCl_2 \cdot 2H_2O$ by means of X-ray analysis and showed that it greatly resembled the structure of NH_4Cl and could be derived from the latter as follows. We take

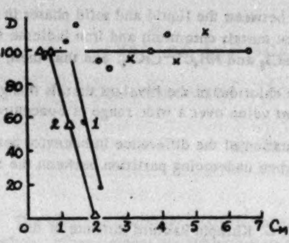


Fig. 1. ● = Fe; Δ = Cr; X = Mn; O = Cu.

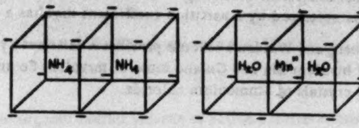


Fig. 2.

two elementary cells of NH_4Cl having a common plane and consisting of 12 chloride ions and 2 ammonium ions disposed at the centers of the two elementary cubes taken (Fig. 2). Two elementary cells of NH_4Cl having a common plane and having 12 chloride ions at the corners and 2 ammonium ions at the centers of the cubes are changed little in dimensions and electrical field when the two ammonium ions are replaced by water molecules and a manganous ion is placed in the center of the square of four chloride ions in the plane that is common to the two cells. Greenberg and Walden explain the formation of mixed crystals by the possibility of the replacement of the group $2NH_4^+4Cl^-$ in the NH_4Cl lattice by the complex anion $(MnCl_4 \cdot 2H_2O)^{=}$. If, in fact, such a replacement occurs, then in this case there should not be a lower limit for mixed-crystal formation.

We consider that, if all these considerations are valid for the manganese system, then they should apply also to the copper system, since the radius of a copper ion is such that it may be placed within the ammonium chloride lattice in the same way as the manganese ion. By analogy with manganese, we consider that in the copper system the guest component is the complex anion $(CuCl_4 \cdot 2H_2O)^{=}$ Similar replacements cannot, however, occur in the systems $NH_4Cl-FeCl_3-H_2O$ and $NH_4Cl-CrCl_3-H_2O$, since the complex anions $(FeCl_5 \cdot H_2O)^{=}$ and $(CrCl_5 \cdot H_2O)^{=}$ contain five chlorine atoms, which is one too many. This fact is bound to be reflected in the structure of the mixed crystals.

Although mixed crystals formed by ammonium and ferric chlorides have been studied in various aspects by many workers [6], there are only a few references in the literature to the chromium system. Retgers [8] obtained mixed crystals by crystallizing ammonium chloride from an aqueous solution containing chromic chloride, the latter being trapped by the solid phase in very small amount. Moreover, Johnsen [9] states that ammonium chloride crystallized from a solution containing chromic chloride is green in color. With regard to the double salts formed between ammonium chloride and chromic chloride, Larsson [10] has obtained a salt of composition $NH_4Cl \cdot CrCl_3 \cdot 6H_2O$, and Neumann [11] has prepared the double salt $2NH_4Cl \cdot CrCl_3 \cdot H_2O$ or $(NH_4)_2[CrCl_5 \cdot H_2O]$, which Werner [12] and others represent as $[Cr(H_2O)Cl_5(NH_4)_2]$.

Whereas for the system $NH_4Cl-FeCl_3-H_2O$ many authors have shown convincingly that the guest component is the complex anion $(FeCl_5 \cdot H_2O)^{=}$, this question has not been finally settled for the chromium system. By analogy with iron, however, it may be supposed that the guest component in the chromium system is the complex anion $(CrCl_5 \cdot H_2O)^{=}$, and this view is supported by the similarity in the curves for the dependence of partition coefficient on concentration of microcomponent (iron or chromium) in the solution. Further support is afforded by the results of experiments devised to determine the behavior of two or more microcomponents when simultaneously present in a solution from which anomalous mixed crystals are formed. The experiments showed that the presence of cupric chloride in the solution had no effect on the partition of chromium between liquid and solid phases, whereas the presence of $FeCl_3$ had a substantial effect on the value of the partition coefficient: its mean value was increased by a factor of 2.5. In this connection it should be noted that the form of the curve for the dependence of the partition coefficient on the concentration of microcomponent in the solution remained unchanged. From these considerations it may be concluded that the guest component in the chromium system is the complex anion $(CrCl_5 \cdot H_2O)^{=}$, which is deposited during crystallization on prepared regions of the lattice formed by the isomorphous complex anion $(FeCl_5 \cdot H_2O)^{=}$, this being the reason for the increase in the partition coefficient of chromium.

SUMMARY

1. Data relating to the partition of small amounts of a substance between the liquid and solid phases in systems consisting of ammonium chloride and the chlorides of the tervalent metals chromium and iron indicate that there is a lower limit for the formation of the mixed crystals $NH_4Cl-FeCl_3$ and $NH_4Cl-CrCl_3$, and that these mixed crystals are colloidal in nature.

2. Partition in systems consisting of ammonium chloride and the chlorides of the bivalent metals manganese and copper is characterized by a partition coefficient that has a constant value over a wide range of concentrations.

3. Greenberg and Walden's scheme provides a satisfactory explanation of the difference in behavior between the chdorides of bivalent Mn and Cu and those of tervalent Fe and Cr when undergoing partition between the saturated solution and crystals of ammonium chloride.

Received August 2, 1954

V. G. Khlopin Radium Institute of the
USSR Academy of Sciences

LITERATURE CITED

[1] E. M. Ioffe and B. A. Nikitin. Bull. Acad. Sci. USSR, Div. Chem. Sci., 1942, No. 6, 383.

[2] V. Khlopin and B. Nikitin, Zeit. für phys. Chem., 145, 137 (1929); B. A. Nikitin, Proc. Radium Inst., 1, 76 (1930).

[3] B. A. Nikitin, Papers collected in honor of 50 years' scientific activity of V. I. Vernadsky, Acad. Sci. USSR Press, 1936.

[4] V. G. Khlopin, Proc. Radium Inst., 4, 34 (1938).

[5] E. M. Ioffe and B. A. Nikitin, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1943, No. 3, 191.

[6] N. S. Kurnakov and N. K. Voskresenskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1937, No. 3, 607; E. Bruner and L. Sieg, Z. allg. anorg. Chem., 229, 175 (1936); H. W. Foot and B. Saxton, J. Am. Chem. Soc., 36, 8 (1914); O. Lehman, Molekularphys., 1, 427 (1888).

[7] A. L. Greenberg and G. H. Walden, J. Chem. Phys., 8, 645 (1940).

[8] I. W. Retgers, Z. phys. Chem., 9, 390, 385 (1892).

[9] A. Johnsen, Neues Jahrb. Minil., 113 (1903).

[10] N. Larsson, Z. anorg. Chem., 110, 153 (1920).

[11] G. Neumann, Ann., 244, 339 (1888).

[12] A. Werner and A. Gubster, Ber., 34, 1603 (1901).

SURFACE AND SORPTION PROPERTIES OF ACTIVE CARBONS

COMMUNICATION 1. SORPTION ISOTHERMS FOR BENZENE AND WATER VAPOR

M. M. Dubinin and E. D. Zaverina

The results of chemical analysis show that the organic matter present in active carbons consists essentially of carbon. When carbons are subjected to activation or thermal treatment at sufficiently high temperatures, the carbon content may attain 98-99%.

When kept and applied under the usual conditions, active carbons are in contact with air and are to some extent moist. As a result of activated adsorption and chemisorption of oxygen, at the surface of the carbon there are chemically bound oxygen atoms, which form surface oxides, the composition and properties of which depend on the temperature conditions of the interaction of oxygen with the carbon [1-3]. With prolonged keeping, slow oxidation of the surface continues with formation of acidic surface oxides [4]. According to the experiments of Pierce and coworkers, active carbons slowly react with sorbed water with formation of surface oxygen complexes [5].

From these observations we may conclude that under normal conditions the surface of active carbons does not consist only of carbon atoms, but is oxidized to some extent. In the oxidation a condition of equilibrium is probably not attained, and slow further oxidation of the active-carbon surface will occur. The final oxidation product, carbon dioxide, is gradually desorbed from the carbon.

In the general case, the sorption of vapors by active carbons depends on the chemical nature and porous structure of the adsorbent. The effect of surface oxides on the sorption of vapors by active carbons has been studied by Bruns [6] and by us [7, 8]. The polar properties of the surface oxides, which behave like unimolecular layers, affect the components of the adsorption forces in different ways. As our experiments [7] show, the surface oxides have an insignificant effect on the dispersional interaction of the molecules of nonpolar substances such as benzene with the carbon surface. In the adsorption of polar molecules such as methanol and water, however, the surface oxides modify the character of the adsorption considerably in the initial sections of the isotherm, particularly when dispersion forces play a relatively small part in adsorptional interaction. The most notable example is provided by the adsorption of water vapor on active carbons [9].

One of the methods of studying the effect of the nature of the surface of the adsorbent on adsorption is based on varying the chemical nature of the surface of the active carbon while maintaining its porous structure practically unchanged. A study of sorption over a wide range of equilibrium pressures, right up to saturation, makes it possible, in principle, to evaluate the relative values of the surface coverage and pore volume in the sorption of water vapor. The slow change in the chemical nature of the surface of the carbon resulting from its oxidation also has a certain practical interest, since it may be associated with the changes occurring in the sorption properties of active carbons during keeping.

These considerations make it necessary to carry out further, more systematic investigations in this field. In the present investigation we have attempted to determine in greater detail the dependence of the sorptive properties of active carbon on the extent of the oxidation of its surface, the structure of the carbon being maintained practically constant.

EXPERIMENTAL

1. The active carbon taken for investigation was granulated material obtained under laboratory conditions from coal; it had a bulk density of Δ = 0.640 g/cc and an ash content of 15.98%. The carbon was ground, and the fraction of grains retained during sieving between sieves having circular openings 1.25 and 1.50 mm in diameter, respectively, was used for the preparation of oxidized carbons (Carbon A).

The main object of the investigation was a study of the sorptive properties of carbons having different amounts of acidic surface oxides, but practically constant in porous structure. As the oxidation of a carbon with atmospheric oxygen is accompanied by a substantial combustion loss, which results in changes in structure, there was no point in comparing the properties of the original active carbon A and its oxidation products. A carbon having no acidic surface oxides and close in structure to the oxidized carbon may be prepared by thermal treatment of the latter in a vacuum at about 1000° [7].

Samples of oxidized carbons were prepared both from the original ash-containing carbon A and also from carbon freed from ash by double treatments with hydrochloric and hydrofluoric acids followed by careful washing with distilled water until the reaction for chloride was negative. The carbon, after drying, had an ash content of 0.61%. After a repeat of this cycle of treatments with hydrochloric and hydrofluoric acids and careful washing, the dried carbon had an ash content of 0.16% (Carbon B).

The carbons A and B were oxidized at 450° with moist air (humidified by passage through a Drechsel bottle containing water) in the rotating retort already described [10]. A 3 g sample of carbon was taken, and the rate of passage of air was 6 cc per minute per gram of carbon. By variation of the length of treatment it was possible to obtain samples of carbon having different contents of acidic surface oxides (Shilov carbon oxides).

An index of the amount of acidic surface oxides formed was provided by the extent to which caustic soda was adsorbed from aqueous solution To measure this adsorption 10 ml of 0.023 N NaOH was added to a 0.4 g sample of the carbon contained in a test tube fitted with a ground stopper. The mixture was agitated for one hour and then centrifuged, and the equilibrium concentration of the solution c was determined by titration to phenolphthalein. The extent of adsorption was expressed in relative units, namely, as the percentage change in the concentration:

$$a = \frac{(c_0 - c)}{c_0} \cdot 100\%, \tag{1}$$

(c_0 is the initial concentration of the solution).

In order to decompose the acidic surface oxides, a sample of oxidized carbon was heated at 950° in a silica tube closed at one end and evacuated down to a few microns of mercury by means of an oil pump. Air was admitted to the tube only after the carbon had cooled. The duration of the thermal treatment of the carbon was established experimentally with the aid of the following experiments. For the oxidized carbon A1 the alkali adsorption was 33.3%. Heating of the carbon for one hour lowered the alkali adsorption to 1.33%, and heating for two hours lowered it to less than 0.01%. On the basis of these preliminary experiments, all samples of oxidized carbon were heated for two hours. The carbons obtained were preserved in sealed glass test tubes.

The principal data relating to the carbons investigated are presented in Table 1.

TABLE 1

Conditions of Preparation and Designation of the Carbon Samples

Original carbon	Air oxidation of carbon at 450°				Thermal treatment of carbon at 950°		Designation of carbon obtained
	time t (hours)	combustion loss ω (%)	relative reactivity β (hour⁻¹)	adsorption of NaOH (%)	yield of carbon (%)	adsorption of NaOH (%)	
A	2.0	10.3	0.052	33.3	—	—	A1
A	3.5	18.7	0.053	45.7	—	—	A2
A1	—	—	—	—	90	0.00	A3
A2	—	—	—	—	90	0.00	A4
B	1.5	9.3	0 062	46.8	—	—	B1
B	2.7	22.3	0.082	56.7	—	—	B2
B1	—	—	—	—	85	0.00	B3
B2	—	—	—	—	85	0.00	B4

The rate of combustion of the carbon in the oxidation process is characterized by the relative reactivity β:

$$\beta = \frac{\omega}{t} \text{ hour}^{-1} \tag{2}$$

(ω is the combustion loss of the carbon as a fraction, and t is the duration of oxidation in hours).

The experimental results show that carbon B, which had been freed from ash, was appreciably more reactive to oxygen at 450° than the original carbon A. It is probable that in this case the removal of ash results in some increase in porosity, leading to enhanced reactivity; the ash components themselves are without appreciable catalytic action in the oxidation process.

The oxidation of carbon with atmospheric oxygen at 450°, which is associated with a substantial combustion loss (up to 20% in our experiments), results in the formation of acidic surface oxides, which, as a result of hydration, form surface carboxyl groups. The presence of these groups is the cause of the adsorption of alkali by ion exchange (H^+ exchanged for Na^+). The adsorptive power of oxidized carbons with respect to caustic soda increases with increase in the combustion loss of the carbon and is appreciably higher for oxidized carbons obtained from de-ashed carbon.

According to the data in Table 1, when oxidized carbons are treated in a vacuum at 950° with the object of breaking down the acidic surface oxides, the carbons lose 10 to 15% in weight, i.e., there is a peculiar sort of combustion loss. At first sight such combustion losses appear excessively high, but they are in accord with the results of one of our earlier investigations [3].

According to elementary analysis, 2.8% of oxygen was present in an active carbon obtained from sugar (sample No. 23 in the paper cited), which was prepared at a fairly high temperature (1000°) by activation with carbon dioxide until the combustion loss was 48%. When this carbon was oxidized with atmospheric oxygen at 500° until the combustion loss was about 15% (sample No. 26), the oxygen content was raised to 11.7%. Acidic surface oxides were formed on the carbon, and these caused a considerable adsorption of caustic soda from aqueous solution (1.61 millimoles per gram at an equilibrium concentration of 100 millimoles per liter).

When the carbon was treated at 950° in a vacuum, much of the oxygen chemically bound in the form of surface oxides was removed as carbon dioxide. If it is assumed that the product of the thermal treatment contained its original amount of oxygen (2.8%), then it is easy to calculate the algebraic loss in weight of the carbon in the thermal treatment (12.7%). This estimated value is within the limits of the range of "combustion losses" of the carbon samples studied.

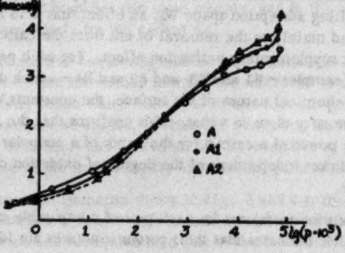


Fig. 1. Isotherms for the sorption of benzene vapor at 20° (semilogarithmic plot) for the carbons: O = A; O = A1; Δ = A2.

The thermal treatment of oxidized carbons in a vacuum at 950° for two hours results in almost complete breakdown of the acidic surface oxides. The amount of alkali adsorbed becomes immeasurably small (less than 0.01%). As later experiments show, the porous structures of the oxidized carbon and the product of its thermal treatment do not differ to an appreciable extent.

2. As an example of a nonpolar vapor we chose the vapor of benzene. We measured the sorption isotherms for benzene vapor at 20° by the sorption-balance vacuum method over a wide range of equilibrium pressures [11]. The preliminary degassing of the carbons was carried out at 450° with evacuation by a three-stage mercury pump over a period of seven hours. At the end of this period the mercury "stuck" in the capillary of the McLeod gage.

In their general character, the sorption isotherms for benzene vapor adsorbed on carbons of series A and B differed little from the isotherm for the original carbon A, particularly in the region of low and medium equilibrium pressures. At higher equilibrium pressures, however, the further activation of the carbons by atmospheric oxygen in the oxidation process causes a substantial increase in the sorption.

By way of example, adsorption isotherms are shown in Fig. 1 as semilogarithmic plots for the original active carbon A (and products A1 and A2), of its activation to different combustion losses. As a result of oxidation there is an appreciable change in the sorptive properties of the carbon, which is associated with change in porous structure. On the other hand, the thermal breakdown of the acidic surface oxides at 950° permits us to convert carbons A1, A2, B1, and B2 into A3, A4, B3, and B4, which have a normal condition of surface, do not contain acidic surface oxides, and have practically identical sorptive properties with respect to benzene vapor. As a typical example we compare the sorption isotherms for carbons B1 and B3 (Fig. 2). We may conclude that the isotherms for the de-ashed carbons of series B coincide completely. In the case of the ash-containing carbons of Series A there is a slight but measurable difference between samples having acidic surface oxides and the corresponding samples having a normal condition of surface.

The active carbons of series A and B are adsorbents of the first structural type, containing relatively fine micropores having fairly high adsorption potentials [12]. For such carbons the following adsorption isotherm is applicable:

$$a = \frac{W_0}{v} e^{-B\frac{T^2}{\beta^2}(\log p_s/p)^2} \qquad (3)$$

(W_s and B are constants of the equation, $\underline{v}$ is the volume of a millimole of the substance being adsorbed in the liquid state, and β is the affinity coefficient). For benzene, which is taken as the standard vapor, $\beta = 1$. Table 2 gives the constants of Equation 3 for the original carbon A and the samples of active carbon of series B.

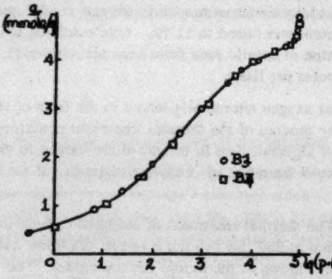


Fig. 2. Isotherms for the sorption of benzene vapor at 20° (semilogarithmic plot) for the carbons: O = B3; □ = B4.

TABLE 2

Constants of the Adsorption Isotherm Equation

Carbon	W_s (cc/g)	$B \cdot 10^6$	Range of applicability (p/p_s)
A	0.281	0.961	$5 \cdot 10^{-5}$–0.2
B1	0.370	1.10	$3 \cdot 10^{-5}$–$2 \cdot 10^{-2}$
B3	0.350	1.09	$3 \cdot 10^{-5}$–$4 \cdot 10^{-2}$
B2	0.345	1.10	$3 \cdot 10^{-5}$–$6 \cdot 10^{-3}$
B4	0.350	1.09	$3 \cdot 15^{-5}$–$4 \cdot 10^{-2}$

As compared with the original carbon A, all of the de-ashed carbons of series B have an appreciably higher limiting adsorption space W_s, an effect that is to be attributed mainly to the removal of ash from the carbon and to a supplementary activation effect. For each pair of carbon samples – B1 and B3, and B2 and B4 – which differ in the chemical nature of the surface, the constants W_s and B are very close in value. This confirms that the adsorptive power of a carbon for the vapor of a nonpolar substance is almost independent of the degree of oxidation of its surface.

The almost exact coincidence of the benzene-vapor sorption isotherms for each pair of comparable carbon samples, i.e., A1 and A3, A2 and A4, B1 and B3, and B2 and B4, indicates that their porous structures are identical to a sufficiently close approximation. It follows that, to the same degree of approximation, the volumes of the micropores and transitional pores are the same for the two members of each pair.

3. As an example of a polar vapor we chose water In the gas state water molecules are not associated; in the liquid state association occurs mainly as a result of the formation of hydrogen bonds between the molecules.

The sorption and desorption isotherms were measured for water vapor at 20° by the sorption-balance vacuum method. The conditions used in the preliminary degassing of the active carbons did not differ from those used in the experiments with benzene vapor. In Figs. 3 and 4 we give, by way of example, the sorption and desorption isotherms for water vapor on the oxidized carbons A2 and B2 and on the corresponding thermally treated samples, the acidic surface oxides of which have been broken down (A4 and B4, respectively). The isotherms for the carbons A1, A3 and B1, B3 are similar in character.

For all of the carbons studied the sorption and desorption isotherms are S-shaped. The first part of the sorption branch of the sorption isotherm for the oxidized carbons A2 and B2, which is concave and extends to $\underline{p/p_s}$ = = 0.4, rises fairly steeply, indicating relatively high adsorption, even in the region of low equilibrium pressures. In the region of medium relative pressures (0.4-0.6), there is a steeper, almost linear rise of adsorption with pressure.

In the region of high relative pressures (0.6-1.0) the isotherm becomes somewhat less steep, although the extent of adsorption still increases fairly rapidly with rise in pressure.

For the carbon samples A4 and B4, which are analogous in porous structure but do not contain acidic surface oxides, the extent of adsorption in the initial region (relative pressures up to 0.4) is small, being at the limit of measurement. As the pressure rises above p/p_s = 0.45, there is a sharp rise in the sorption branch, which then has a long linear portion. As the carbon approaches a state of saturation, the curve becomes somewhat less steep. The limiting sorption at a relative pressure of unity is substantially lower for carbons freed from acidic surface oxides.

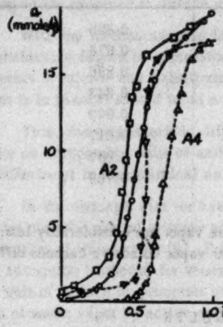


Fig. 3. Sorption and desorption isotherms for water vapor at 20° on carbons A2 and A4.

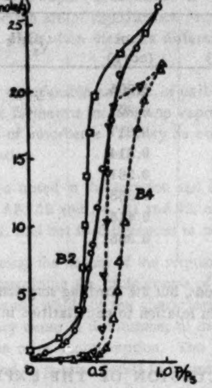


Fig. 4. Sorption and desorption isotherms for water vapor at 20° on carbons B2 and B4.

For all of the carbons studied the desorption branches of the isotherms are, in general, analogous in form to the sorption branches in the regions of medium and high relative pressures. However, the almost linear portions of the desorption branches rise more steeply, and in the range of relative pressures from 0.7 to 1.0 the curves are less steep, particularly for the carbon A4.

For the ash-containing carbons A1, A3 and A2, A4 there is marked irreversibility in the initial region of the isotherm. When the carbon samples are subjected to a vacuum at 20°, they retain an appreciable amount of the more firmly bound water. Removal of ash does not greatly reduce the irreversibility of the sorption, particularly for the samples B3 and B4. Unlike the adsorption isotherms for active carbons derived from sugar, those for the carbons of series A and B have no initial reversible section. The residual ash content of about 0.2% is probably the source of the irreversibility of the initial parts of the isotherms for carbons of series B.

From the isotherms shown in Figs. 3 and 4 it may be concluded that oxidation of the surface of the carbon with formation of acidic surface oxides results in a displacement of the almost linear sections of the main rise in the sorption and desorption branches of the isotherms into the region of lower relative pressures. Breakdown of the acidic surface oxides without substantial change in the porous structure of the carbon results in considerably lower limiting sorption values.

In conclusion, it is of interest to compare the limiting sorption volumes for water vapor $V_s^{H_2O}$ with the volumes of the micropores of the carbons and with the sums of the volumes of the micropores and transitional pores, which, by definition, are the limiting sorption volumes for benzene vapor $V_s^{C_6H_6}$ [13]. The limiting sorption volumes were calculated from the formula:

$$V_s = a_s \cdot V. \tag{4}$$

(a_s mmoles/g is the limiting sorption at p/p_s = 1 and V is the volume of 1 mmole of the substance being adsorbed, in the liquid state). The comparison of these quantities is made in Table 3.

The data in Table 3 show that, for the carbon samples A3, A4, B3, and B4, which do not contain acidic surface oxides, the limiting sorption volumes for water vapor coincide with the volumes of the micropores of the active carbons within the limits of experimental error. We have stressed this conclusion in several of our papers [8]. For the oxidized carbons A1, A2, B1 and B2, the limiting sorption volumes for water vapor exceed the volumes of

TABLE 3

Comparison of the Limiting Sorption Volumes of Water Vapor with the Volumes of the Pores of the Active Carbons

Carbon	$a_s^{H_2O}$ (mmole/g)	$V_s^{H_2O}$ (cc/g)	V_{mi} (cc/g)	$V_s^{C_6H_6} = V_{mi} + V_n$ (cc/g)	$V_s^{H_2O}/V_s^{C_6H_6}$
A1	17.59	0.318	0.305	0.356	0.895
A3	17.05	0.308	0.304	0.351	0.878
A2	18.90	0.342	0.317	0.382	0.896
A4	17.15	0.310	0.314	0.368	0.843
B1	22.31	0.403	0.361	0.446	0.903
B3	19.78	0.357	0.368	0.438	0.817
B2	26.38	0.476	0 415	0.526	0.897
B4	21.90	0.396	0.396	0.503	0.788

the micropores of the active carbons, but the limiting sorption volumes for benzene vapor are considerably less. These results are of significance in relation to peculiarities in the sorption of water vapor on active carbons differing in the nature of their surfaces.

DISCUSSION OF THE EXPERIMENTAL RESULTS

The main object of the present investigation was the determination of the effect of the chemical nature of the surface of active carbons on their sorption properties for an example of a nonpolar vapor, benzene, and for an example of a polar vapor, water, which is able to undergo intermolecular hydrogen bonding. Since adsorption and capillary-condensation processes depend very greatly on the porous structure of the active carbons [8, 14], it was of fundamental importance to compare the sorption properties of carbons differing in the nature of their surfaces but identical in porous structure This extremely complex experimental problem can, of course, be solved only within a certain approximation.

The surface of an active carbon prepared at a high temperature in absence of an oxidizing atmosphere and brought after cooling into contact with atmospheric oxygen contains oxygen atoms taken up by activated adsorption, which, according to Shilov, form surface oxides of a basic character [1]. For us the details of the structure of these oxides are not of great importance, the only important fact being the presence of chemically bound oxygen atoms on the surface of the carbon, which may be regarded as forming surface oxides that do not give the carbon the power to adsorb inorganic bases (NaOH) from aqueous solution.

Oxidation of the carbon with atmospheric oxygen at 450° results in the formation of surface oxides, which, in the hydrated form, can be regarded as surface carboxyl groups. Simultaneously there is appreciable oxidation of the carbon to carbon dioxide, a measure of which is given by the combustion loss of the carbon. This process is a form of activation of the carbon at a comparatively low temperature, and it results in a change in the porous structure of the carbon as in the usual high-temperature activation with oxidizing gases (CO_2, H_2O). The resulting oxidized carbon has ion-exchange properties and is able to adsorb alkali from aqueous solution as a result of the exchange of H^+ of carboxyls for cations, e.g., Na^+.

The oxidized carbon contains both forms of surface oxides, i.e., the Shilov basic type and the acidic type. These have the character of unimolecular films that do not fully cover the surface. This conclusion follows naturally from an analysis of the comparatively low limiting adsorption values of inorganic basesand acids (up to 1.5 mmoles per gram) when the adsorption of these substances is explained on the ion-exchange scheme.

If the surface oxides are regarded as special sites on the surface of the carbon, then they cannot have any great significance in the adsorption of the vapor of a nonpolar substance such as benzene and will not play the part of active surface regions for this process. This conclusion follows from the very nature of the dispersional interaction of molecules of nonpolar substances and the surface of the carbon. Individual atoms of foreign substances such as oxygen, bound by chemical forces, cannot affect the value of the adsorption potential to any appreciable extent. From this we reach the fundamental conclusion that the surface oxides of the carbon are practically without effect on its adsorption properties with respect to benzene vapor.

Identity of structure in two samples of adsorbents is expressed by identity in specific surface and in pore-volume distribution function. When this condition is fulfilled, the volumes of the different kinds of pores are, of course, equal. Both of the above factors are of determining significance for the adsorption of benzene vapor, the example of a nonpolar substance selected in our investigation. Consequently, identity of the sorption properties of comparable samples of carbons with respect to benzene vapor (coincidence of sorption isotherms) and equality of the volumes of the micro- and transitional pores (which are of significance for sorption equilibrium) form criteria for the identity of porous structure in carbons, even when there are differences in the nature of the surfaces owing to the presence of surface oxides.

With the method adopted for the preparation of comparable samples of carbons we obtained coincidence, to a satisfactory degree of approximation, of the sorption isotherms for benzene vapor and substantial equality in the volumes of micro- and transitional pores for the pairs of adsorbents. It may be considered, therefore, that our problem is in general solved to an acceptable approximation.

Thus, the characteristic differences that we have noted in the sorption and desorption isotherms for water vapor on comparable pairs of active carbons (A1 and A3, A2 and A4, B1 and B3, and B2 and B4) must be attributed to differences in the chemical nature of their surfaces, and not to differences in porous structure.

In the concepts that we have developed concerning the nature of the sorption of water vapor, surface carbon oxides play the part of primary adsorption centers determining the main course of the processes of adsorption and desorption of water vapor [9]. From this point of view the whole of the characteristic difference in the form of the adsorption isotherms for water vapor has its primary cause in the number of oxygen atoms originally taken up per unit of surface by processes of activated adsorption or of chemisorption. The problem of the nature of the sorption of water vapor by active carbons will be examined in greater detail in future communications.

SUMMARY

1. Pairs of samples of active carbon were prepared, each pair being such that the two carbons were very close in porous structure but were distinguished by the presence in one of acidic surface oxides; these oxides were absent in the other, which was freed from them by thermal treatment in a vacuum at about 1000°. It was proved that the samples of carbon chosen for comparison were almost identical in porous structure, although differing in the nature of their surfaces.

2. A study was made of the sorptive properties of carbons with respect to a nonpolar substance, benzene. It was shown experimentally that acidic surface oxides have no appreciable effect on the sorptive power of carbon for benzene vapor over a wide range of equilibrium pressures.

3. The sorption and desorption isotherms of water vapor were investigated for carbons containing acidic surface oxides and for the corresponding carbons freed from these oxides. It was found that the surface oxides had a very considerable effect on the sorptive power of carbons for water vapor, the effect being manifested in the sorption and desorption isotherms of the oxidized carbons by a displacement of the curve in the region of low relative pressure.

4. The basic causes for the differences in the adsorption properties of active carbons differing in the chemical nature of their surfaces were examined.

Institute of Physical Chemistry of the
USSR Academy of Sciences

Received October 26, 1954

LITERATURE CITED

[1] N. A. Shilov, E. G. Shatunovskaya and K. V. Chmutov, Z. Phys. Chem., 149, 211 (1930).

[2] N. A. Shilov, E. G. Shatunovskaya and K. V. Chmutov, Z. Phys. Chem., 150, 31 (1930).

[3] M. M. Dubinin and E. D. Zaverina, J. Phys. Chem., 12, 380 (1938).

[4] E. D. Zaverina and M. M. Dubinin, J. Phys. Chem., 12, 397 (1938).

[5] C. Pierce, R. N. Smith, J. W. Wiley and H. Cordes, J. Am. Chem. Soc., 73, 4551 (1951).

[6] B. Bruns and M. Maksimova, J. Phys. Chem., 4, 554 (1933).

[7] E. D. Zaverina and M. M. Dubinin, J. Phys. Chem., 13, 151 (1939).

[8] M. M. Dubinin and E. D. Zaverina, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 2, 217 [T.p. 175];* Proc. Acad. Sci. USSR, 92, 111 (1953).

---

* T.p. = Consultants Bureau Translation pagination.

[9] M. M. Dubinin, J. Russ. Chem Soc., 62, 1829 (1930).

[10] M. M. Dubinin and E. Sawerina, Acta Physicochimica USSR, 4,647 (1936).

[11] M. M. Dubinin and E. D. Zaverina, J. Phys. Chem., 23, 1129 (1949).

[12] M. M. Dubinin, Jubilee Collection of the Acad. Sci. USSR, Part 1, 562, 1947.

[13] M. M. Dubinin and E. D. Zaverina, J. Phys. Chem., 21, 1373 (1947).

[14] M. M. Dubinin, E. D. Zaverina and L. V. Radushkevich, J. Phys. Chem., 21, 1351 (1947).

REACTION OF VITREOUS SODIUM SILICATES AND ALUMINOSILICATES WITH AQUEOUS SOLUTIONS

COMMUNICATION 7. REACTION OF VITREOUS SODIUM SILICATES AND ALUMINOSILICATES WITH SALT SOLUTIONS

S. K. Dubrovo and Yu. A. Shmidt

In previous communications we have described the interaction of vitreous sodium silicates and aluminosilicates with water and with solutions of acids and alkalis [1-4]. The object of the present work was the determination of the action of solutions of certain salts on these glasses. Such an investigation is of interest because, under the conditions obtaining in practice, the aqueous solutions that act upon glasses and natural minerals will generally contain salts of some kind or other.

Comparatively little study has been devoted to the interaction of glasses with salt solutions. In the course of an investigation into the polishing process, Grebenshchikov [5] studied this problem and noted that the presence of various metal ions in water affects the rate of growth and the physicochemical properties of the siliceous film on the surface of the glass. Schröder [6] studied the attack of solutions of sodium chloride, arsenates, and some other salts on window glass; he found that the destructive effect of caustic soda solutions on glass is intensified by an addition of sodium chloride.

One of the few investigations on the interaction of glasses with solutions of alkaline-earth chlorides is that of Gastev [7], who tried to establish the cause of the increase in the chemical stability of alkali-silicate glasses resulting from an addition of alkaline-earth oxides. With this object he treated glass powders containing 80% by weight of SiO_2 and 20% by weight of Na_2O or K_2O with calcium chloride, magnesium chloride, and barium chloride solutions. He found that the stability of a sodium silicate glass toward water was increased by treatment of the glass with calcium chloride solution. Magnesium chloride and barium chloride solutions did not have this effect. The author's explanation of this behavior is that only those bivalent ions having a radius close to that of the alkali-metal ion in the glass are adsorbed from solution on the siliceous film formed on the surface. As a result of such adsorption, the protective properties of the film are enhanced.

In Gastev's work there are some errors of principle and method. The author tacitly assumes that the state of the alkaline-earth ions absorbed by the film from the solution is the same as if these ions had been present in the glass from the beginning, being introduced in the process of its preparation. This assumption, however, is incorrect, as can be seen from the following and other considerations. It is known that even small additions of any alkaline-earth oxide to an alkali-silicate glass result in a great increase in the chemical stability of the glass [8, 9]. It follows, however, from Gastev's results that the absorption of barium and magnesium ions has no effect at all on the chemical stability of sodium silicate glass, while the effect of calcium ions is comparatively slight. In determining titrimetrically the amount of alkaline oxides passing from the glass to the solution, the author was unable to take into account that part of the alkali-metal ions (e.g., sodium ions) which are displaced into the solution by calcium ions by the ion-exchange reaction:

$$2Na^{+}_{glass} + Ca^{++}_{solution} = Ca^{++}_{glass} + 2Na^{+}_{solution} \qquad (1)$$

and therefore, do not increase the alkali content of the solution. Moreover, the experiments were carried out under conditions that permitted access of carbon dioxide from the air. All these factors, taken together, could seriously distort the results.

We have investigated the interaction of vitreous sodium silicates and aluminosilicates with solutions of sodium, calcium and aluminum chlorides.

EXPERIMENTAL

Interaction of vitreous sodium silicates and aluminosilicates with sodium chloride solutions. A study was made of the interaction of three sodium silicates and three sodium aluminosilicates with N NaCl at 40°. We have described the experimental procedure previously [1, 3]. The results are given in Tables 1 and 2. As before, the symbols $\underline{n}_{Na_2O}$, $\underline{n}_{Al_2O_3}$, and $\underline{n}_{SiO_2}$ represent the amounts of the respective components that pass into solution from 1 cm^2 of the glass surface. The quantities α and β are the proportions of SiO_2 and Al_2O_3, respectively, passing into solution from the layer of glass that is undergoing interaction.

In the experiments with the silicate $Na_2O \cdot 1.7SiO_2$ the presence of sodium chloride in the solution leads to a reduction in the value of $\underline{n}_{Na_2O}$ and to an increase in the rate of dissolution of the siliceous film. Later, however, when the film is completely dissolved, the value of $\underline{n}_{SiO_2}$ is found to be less than in the experiments with water. In this case it is probable that, as in the previously described interaction of silicates with alkaline solutions [4], the rate at which the silica of the glass is dissolved now depends on the primary process of the passage of sodium ions into solution, so that with increase in the concentration of sodium chloride this rate diminishes.

The results of the experiments on the interaction of the other sodium silicates with sodium chloride solution confirm our previous conclusions [10], namely that increase in the concentration of sodium chloride in the solution retards the passage of Na_2O into solution and accelerates the dissolution of the siliceous film. The results that we have obtained for vitreous sodium aluminosilicates point to the same conclusion. In all cases the amounts of alumina passing into solution were very small. At the beginning of the experiments, the presence of sodium chloride in the solution apparently brings about an increase (although this increase is a slight one) in

TABLE 1

Interaction of Vitreous Sodium Silicate of Composition $Na_2O \cdot 1.7SiO_2$ with N Sodium Chloride Solution

Solution	Index	Time (hours)					
		1/4	1/2	1	2	4	6
Water	$\underline{n}_{Na_2O} \cdot 10^{-6}$	14	28	51	104	220	352
	$\underline{n}_{SiO_2} \cdot 10^{-6}$	7.2	15	33	140	350	566
	α	0.30	0.31	0.38	0.79	0.94	0.97
1 N NaCl	$\underline{n}_{Na_2O} \cdot 10^{-6}$	11	22	45	91	187	269
	$\underline{n}_{SiO_2} \cdot 10^{-6}$	15	36	78	157	319	455
	α	0.80	0.96	1.0	1.0	1.0	1.0

TABLE 2

Interaction of Vitreous Sodium Silicates and Aluminosilicates with N Sodium Chloride Solution

Composition	$Na_2O \cdot 2SiO_2$				$Na_2O \cdot 2.3SiO_2$				$Na_2O \cdot 3SiO_2$			
Solution	water		1 N NaCl		water		1 N NaCl		water		1 N NaCl	
Index	time (hours)											
	1	6	1	6	1	6	1	6	1	6	1	6
$\underline{n}_{Na_2O} \cdot 10^{-6}$	19	63	8.2	48	9.1	32	2.9	13	1.6	4.7	0.94	2.5
$\underline{n}_{SiO_2} \cdot 10^{-6}$	3.1	9.3	5.6	77	0.24	1.0	1.0	5.0	0.04	0.08	0.05	0.13
α	0.08	0.08	0.37	0.80	0.011	0.014	0.16	0.17	0.008	0.006	0.019	0.017

Composition	$Na_2O \cdot 0.05Al_2O_3 \cdot 1.7SiO_2$				$Na_2O \cdot 0.05Al_2O_3 \cdot 2SiO_2$				$Na_2O \cdot 0.15Al_2O_3 \cdot 1.7SiO_2$			
Solution	water		1 N NaCl		water		1 N NaCl		water		1 N NaCl	
Index	time (hours)											
	1	6	1	6	1	6	1	6	1	6	1	6
$\underline{n}_{Na_2O} \cdot 10^{-6}$	17	50	6.0	28	8.0	22	3.1	10	2.7	6.3	1.5	4.2
$\underline{n}_{Al_2O_3} \cdot 10^{-6}$	0.010	0.13	0.017	0.043	0.003	0.002	0.005	0.011	–	–	–	–
$\underline{n}_{SiO_2} \cdot 10^{-6}$	2.2	6.6	2.8	21	0.22	1.2	0.44	1.6	–	–	–	–
α	0.076	0.078	0.27	0.44	0.014	0.027	0.071	0.080	–	–	–	–
β	0.012	0.052	0.057	0.031	0.008	0.018	0.032	0.022	–	–	–	–

the amounts of alumina passing into solution, but these amounts are later less than in the experiments with water. As we have shown previously [3], in the interaction of sodium aluminosilicates with water, part of the aluminum ions are adsorbed by the residual film from the solution. An analogous phenomenon is observed also in experiments with sodium chloride solution. In experiments with water it was found that the amount of adsorbed aluminum ions is greater when the original glass is less stable, i.e., when the structure of the residual surface film is more open. Correspondingly, the enhanced breakdown of the residual film resulting from the action of sodium chloride solution – which will probably make the structure of the film more open – will facilitate the adsorption of aluminum ions on the surface. This is probably the explanation of the fact that in the experiments with sodium chloride solution the value of β does not increase with time, but diminishes.

The presence of sodium chloride in the solution increases also the rate of dissolution of quartz glass in caustic alkalis. Thus, whereas for the action of a solution containing only caustic soda the value of $\underline{n}_{SiO_2}$ for 1 hour is $0.9 \cdot 10^{-8}$ mole/cm² in a 0.01 N solution and $2.4 \cdot 10^{-8}$ mole/cm² in a 0.1 N solution, in a solution containing also sodium chloride at normal concentration the corresponding values of $\underline{n}_{SiO_2}$ are $1.4 \cdot 10^{-8}$ and $2.9 \cdot 10^{-8}$ mole/cm². Hence, increases in the concentrations of alkali and sodium chloride have the same effect on the rate of dissolution of quartz glass as on the rate of dissolution of the siliceous films on the surface of vitreous sodium silicates and aluminosilicates. As we have already indicated [4], on the surface of quartz glass there may be Si–OH groups, which are capable of participating in ion exchange. It is possible that a similar type of exchange adsorption of sodium ions at the surface may have the same role for quartz glass as that played for other glasses by increase in the concentration of sodium ions in the layer of the siliceous film at the interface with the solution.

TABLE 3

Interaction of Vitreous Sodium Silicates with Calcium Chloride Solutions

Composition	Solution	Index	Time (hours)				
			½	1	2	4	6
$Na_2O \cdot 2SiO_2$	Water	$\underline{n}_{Na_2O} \cdot 10^{-6}$	11	18	30	47	62
		$\underline{n}_{SiO_2} \cdot 10^{-6}$	2.3	3.2	4.2	5.8	9.3
	0.01 N $CaCl_2$	$\underline{n}_{Na_2O} \cdot 10^{-6}$ (c)	9.2	14	24	41	52
		$\underline{n}_{Na_2O} \cdot 10^{-6}$ (t)	9.4	14	26	29	34
		$\underline{n}_{SiO_2} \cdot 10^{-6}$	0.15	0.22	0.46	0.59	0.74
	0.1 N $CaCl_2$	$\underline{n}_{Na_2O} \cdot 10^{-6}$ (c)	8.1	14	22	36	46
		$\underline{n}_{Na_2O} \cdot 10^{-6}$ (t)	8.4	14	20	26	30
		$\underline{n}_{SiO_2} \cdot 10^{-6}$	0.07	0.13	0.19	0.24	0.32
	0.2 N $CaCl_2$	$\underline{n}_{Na_2O} \cdot 10^{-6}$ (c)	8.5	14	26	39	47
		$\underline{n}_{Na_2O} \cdot 10^{-6}$ (t · without CO_2)	8.1	14	25	37	41
		$\underline{n}_{Na_2O} \cdot 10^{-6}$ (t)	7.9	13	22	28	–
		$\underline{n}_{SiO_2} \cdot 10^{-6}$	0.07	0.21	–	0.22	0.30
$Na_2O \cdot 2.3SiO_2$	Water	$\underline{n}_{Na_2O} \cdot 10^{-6}$	5.1	9.1	15	25	32
		$\underline{n}_{SiO_2} \cdot 10^{-6}$	0.12	0.24	0.54	0.83	1.0
	0.1 N $CaCl_2$	$\underline{n}_{Na_2O} \cdot 10^{-6}$ (c)	4.4	7.4	11	18	24
		$\underline{n}_{Na_2O} \cdot 10^{-6}$ (t)	4.5	7.2	11	11	9
		$\underline{n}_{SiO_2} \cdot 10^{-6}$	0.08	0.10	0.16	0.16	0.12
$Na_2O \cdot 3SiO_2$	Water	$\underline{n}_{Na_2O} \cdot 10^{-6}$	–	1.6	2.5	3.6	4.7
		$\underline{n}_{SiO_2} \cdot 10^{-6}$	–	0.040	0.046	0.065	0.078
	0.1 N $CaCl_2$	$\underline{n}_{Na_2O} \cdot 10^{-6}$ (c)	–	1.3	2.0	3.1	3.9
		$\underline{n}_{Na_2O} \cdot 10^{-8}$ (t)	–	1.1	0.6	0.4	–
		$\underline{n}_{SiO_2} \cdot 10^{-6}$	–	0.033	0.025	0.024	0.024

Note: (c) indicates values of $\underline{n}_{Na_2O}$ obtained colorimetrically; (t) indicates titration in presence of CO_2 of the air; (t without CO_2) indicates titration in absence of CO_2.

Interaction of vitreous sodium silicates with calcium chloride solutions. The interaction of four sodium silicates with calcium chloride solutions was studied. The experiments were carried out at 40°. In most of the experiments the concentration of calcium chloride was 0.1 N, but for sodium disilicate experiments were carried out also with 0.01 and 0.2 N solutions. The calcium chloride solutions were prepared by the dilution of a stock 5 N solution of calcium chloride to the required concentration with distilled water, which was previously boiled in a silver beaker to remove CO_2 and then cooled rapidly. As ourrmain means for the determination of Na_2O in solution we selected a colorimetric method, which gives the total amount of sodium in the solution. We also titrated the solution. The results of the experiments are given in Table 3. In the experiments with the silicate $Na_2O \cdot 1.7SiO_2$, spongy growths formed on the surface of the sample; on the outside of these there were white flocks (apparently $CaCO_3$), and underneath there were semitransparent formations containing silica. The results of these experiments are, therefore, not comparable with those of the other experiments.

In the experiments with vitreous sodium disilicate the presence of calcium chloride in the solution reduced the values of $\underline{n}_{Na_2O}$ to approximately the same extent as the corresponding concentrations (0.01 and 0.1 N) of sodium chloride did [10]. At the beginning of the experiment (in the first 1-2 hours) the amounts of Na_2O found in the solution by the two methods coincided within the limits of experimental error. After two hours the amounts of Na_2O determined colorimetrically were appreciably higher than those found by titration. At about the same time a white substance made its appearance on the surface of the solution. This substance was found to be calcium carbonate, the formation of which by the reaction

$$CaCl_2 + 2NaOH + CO_2 = CaCO_3 + 2NaCl + H_2O \qquad (2)$$

led to the removal from the solution of part of the alkali that had passed into it and so to the difference between the values of $\underline{n}_{Na_2O}$ found by titration and the values determined colorimetrically.

In order to avoid absorption of CO_2 from the air in the experiments with 0.2 N $CaCl_2$, the beaker containing the solution was closed with a silver cover provided with hydraulic seals for a stirrer and two tubes. Tests were taken through one of the tubes, and through the other air freed from CO_2, was passed over the surface of the solution. The previously prepared solution was boiled in a silver beaker to remove carbon dioxide, brought to the original volume (by weighing), and cooled with the cover in position without access of carbon dioxide. When this procedure was adopted, the discrepancies between the values of $\underline{n}_{Na_2O}$ obtained colorimetrically and by titration were within the limits of experimental error. The somewhat lower values obtained by the titration method at the end of the experiment may indicate slight absorption of calcium ions by the siliceous film in accordance with the reaction (1) In any case, in order of magnitude this absorption is not greater than $3 \cdot 10^{-6}$ mole/cm². The amount of silicic acid found in the solution was considerably less in the experiments with calcium chloride solutions than in the experiments with water. As in previous work, control experiments were made on the determination of silicic acid in solution after it had been converted into a molecularly dispersed state. The results of these determinations give us reason to consider that the greater part, if not all, of the silicic acid is present in solution in a molecularly dispersed state.

In the interaction of the silicates $Na_2O \cdot 2.3SiO_2$ and $Na_2O \cdot 3SiO_2$ with calcium chloride solutions, the values of $\underline{n}_{Na_2O}$ were again found to be lower than in the experiments with water. During the first two hours of the experiments with $Na_2O \cdot 2.3SiO_2$ the amount of Na_2O found in the solution by titration was almost identical with the amount found colorimetrically, indicating that in this case the amount of CaO absorbed did not exceed $2 \cdot 10^{-7}$ mole/cm². Later, however, the values of $\underline{n}_{Na_2O}$ found by titration not only did not increase, but even began to diminish. For both silicates the amounts of silicic acid found in solution in parallel experiments varied greatly (by as much as ± 30% from the mean value). Also, toward the end of the experiment $\underline{n}_{SiO_2}$ even began to fall in value.

Microscopic investigation of the scum formed on the surface of the solution during the experiments showed that it consisted of crystals of two modifications of calcium carbonate — calcite (large rhombic crystals having a refractive index of 1.658) and aragonite. Exactly similar crystals were formed on the surface of a solution of calcium chloride to which alkali had been added, when this was kept under conditions analogous to those of the experiments. Spectrum analysis of the scum showed that it contained only traces of silicic acid. Crystals of calcite were detected also on the surface of samples of the investigated silicates after experiments conducted in presence of atmospheric carbon dioxide. After treatment of a silicate of composition $Na_2O \cdot 4SiO_2$ — which was investigated also by Gastev [7] — with 0.01 N $CaCl_2$ for one hour at 60° (the conditions of one of Gastev's experiments), a large number of fine crystals were found on the surface of the sample. When we increased the duration of the experiment to six hours, we obtained fairly large crystals of calcite on the surface of the sample (see figure).

In experiments with sodium disilicate conducted in absence of carbon dioxide, formation of calcium carbonate was not detected. When, however, the sample was taken from the solution and placed under the microscope, the formation of very fine calcite crystals could be detected already after 5-10 minutes. In the course of this time an appreciable amount of scum formed on the surface of the solution.

It will be clear from the results described that the interaction of vitreous sodium silicates with calcium chloride solutions is considerably more complex than the processes occurring when only univalent sodium and hydrogen ions are present in solution. On the basis of the high valency of calcium ions as compared with sodium ions, it might be expected that the former would be vigorously absorbed by the residual film and would, therefore, have a much greater retarding action on the rate at which Na_2O passes into solution. Actually, however, the retarding action of calcium chloride solutions was found to be approximately the same as that of sodium chloride solutions of the corresponding concentrations. Moreover, when the concentration of calcium ions is increased from 0.01 to 0.2 N, their retarding action remains practically unchanged. It may, therefore, be supposed that calcium ions do not penetrate deeply into the siliceous film, but are merely adsorbed on its surface. This view is confirmed by findings reported in the literature, namely, that calcium ions enter a glass surface during electrolysis only with difficultly [11] and that they have practically no effect on the potential of a glass electrode [12]. Nevertheless, the appreciable reduction in the values of $\underline{n}_{SiO_2}$, as compared with the values obtained for water, indicates that small amounts of calcium ions are adsorbed on the surface of the film, thus retarding its dissolution.

TABLE 4

Interaction of Vitreous Sodium Disilicate with Aqueous Solutions Containing Aluminum Salts

Solution	Index	Time (hours)				
		1	2	4	6	8
Water	$\underline{n}_{Na_2O}\cdot 10^{-6}$	18	30	47	62	76
	$\underline{n}_{SiO_2}\cdot 10^{-6}$	3.2	4.2	5.8	9.3	13
	a	0.09	0.07	0.06	0.08	0.09
0.003 N AlCl$_3$	$\underline{n}_{Na_2O_2}\cdot 10^{-6}$	22	32	49	65	83
	$\underline{n}_{SiO_2}\cdot 10^{-6}$	0.71	0.98	1.4	3.4	5.1
	a	0.016	0.015	0.015	0.026	0.030
0.01 N HCl	$\underline{n}_{Na_2O}\cdot 10^{-6}$	23	40	76	87	102
	$\underline{n}_{SiO_2}\cdot 10^{-6}$	0.08	0.20	0.66	2.1	4.6
	a	0.002	0.003	0.004	0.012	0.022
0.01 N HCl + 0.003 N AlCl$_3$	$\underline{n}_{Na_2O}\cdot 10^{-6}$	24	5	75	93	115
	$\underline{n}_{SiO_2}\cdot 10^{-6}$	0.10	0.11	0.26	0.55	0.72
	a	0.002	0.001	0.002	0.003	0.003
0.01 N KOH	$\underline{n}_{Na_2O}\cdot 10^{-6}$	4.9	12	28	50	64
	$\underline{n}_{SiO_2}\cdot 10^{-6}$	2.7	7.9	40	72	109
	a	0.24	0.32	0.70	0.72	0.84
0.01 N KOH + 0.003 N AlCl$_3$	$\underline{n}_{Na_2O}\cdot 10^{-6}$	11	21	32	38	48
	$\underline{n}_{SiO_2}\cdot 10^{-6}$	0.74	2.0	3.7	6.2	9.4
	a	0.034	0.048	0.057	0.081	0.10

In the interaction of vitreous sodium silicates with calcium chloride solution, several secondary processes may occur which complicate the general picture of the phenomenon, for example, the formation of a precipitate of calcium carbonate Moreover, in some experiments we observed a reduction in the concentration of silica with time, but we did not succeed in finding the cause of this effect because the concentrations of the solutions were very low. Our results show that precipitation of calcium carbonate from solution could have occurred also in Gastev's work [7]. In work with powders such precipitation could (and apparently did) remain unnoticed, so that the observed effect of increased stability could be overestimated.

Interaction of Vitreous Sodium Disilicate with Aluminum Chloride Solution. Experiments were carried out on the interaction of vitreous sodium disilicate with water, 0.01 N HCl, and 0.01 N KOH in presence of aluminum chloride at 40°. The results are given in Table 4. In an acid medium and in water the presence of aluminum chloride in the solution had little effect on the rate at which Na_2O passed into solution. In an alkaline medium the rate at which sodium ions passed from the glass to the solution in presence of aluminum chloride rose at first, and then fell. It is interesting to note that the incorporation of alumina in vitreous sodium silicates lowers the rate at which sodium ions pass from the glass to the solution — this fact has been established in our previous investigations. The mechanism of the action of the aluminum ions present in the solution is thus quite different. This again confirms the conclusion reached above, namely, that it is incorrect to make inferences relating to the part played by ions in the glass from a study of the action of aqueous solutions containing these ions on glass.

As can be seen from Table 4, addition of aluminum chloride to water and to 0.01 N solutions of acid and alkali greatly diminishes the rate at which silica passes from the glass to the solution. In this respect the effect of aluminum chloride is analogous to that of calcium chloride. The process of breakdown of vitreous sodium disilicate by solutions of aluminum salts can be represented as proceeding in two stages. The first stage is the exchange of sodium ions from the glass for hydrogen ions from the solution, so that a siliceous film is formed at the surface. This film, and also, possibly, partially dissolved silica, then interacts with aluminum salts — or, in an alkaline medium, with aluminates — with formation of difficultly soluble colloidal hydrated aluminosilicates at the surface. As is well-known, reactions between silicic acid and solutions of aluminates proceed readily with formation of permutites[13]. When aqueous solutions containing aluminum ions interact with vitreous silicates, it may be expected that analogous aluminosilicates will form at the surface of the glass. As a result of the effects discussed we observe a reduction in the rate of breakdown of sodium disilicate when aluminum salts are introduced into the solution.

SUMMARY

1. The interaction of vitreous sodium silicates and aluminosilicates with solutions of sodium, calcium, and aluminum chlorides was studied.

2. It was found that, with increase in the concentration of sodium chloride in the solution, there was a reduction in the rate at which Na_2O passed from the glass into the solution and an increase in the rate at which silicic acid passed into the solution.

3. It was shown that, when vitreous sodium silicates interact with calcium chloride solutions in presence of carbon dioxide, secondary processes occur with the formation of precipitates of calcium carbonate.

4. It was shown that in treatments with calcium chloride and aluminum chloride solutions the breakdown of the silica skeleton of silicate glasses is greatly retarded.

Received November 15, 1954

Institute of Silicate Chemistry of the
USSR Academy of Sciences

LITERATURE CITED

[1] S. K. Dubrovo and Yu. A. Shmidt, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, No. 4, 597 [T.p. 535].*

[2] S. K. Dubrovo, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 5, 770 [T.p. 661].*

[3] Yu. A. Shmidt, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 5, 778 [T.p. 669].*

[4] S. K. Dubrovo and Yu. A. Shmidt, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, No. 3, 403 [T.p. 359].*

[5] I. V. Grebenshchikov, Bull. Acad. Sci. USSR, Div. Tech. Sci., No. 1, 3 (1937).

[6] H. Schröder, Glastechn., Ber., 26, 4, 91 (1953).

[7] Yu. A. Gastev, Trans. All-Union Silicate Research Inst., No. 32, 1953.

[8] V. Dimbleby, W. E. S. Turner, J. Soc. Glass Techn., 10, 304 (1926).

[9] J. Ensy, Glastechn., Ber., 5, No. 10, 449; No. 11, 509 (1928).

[10] Yu. A. Shmidt, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 2, 236 [T.p. 191].*

[11] F. Quittner, Ann. Phys., 4, 85, 745 (1928).

[12] B. P. Nikolsky, J. Phys. Chem., 10, 3,435 (1937).

[13] J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. VI, Part III, 1947, p. 577.

---

* T.p. = Consultants Bureau Translation pagination.

Calcite crystals on the surface of a vitreous silicate of composition $Na_2O \cdot 4SiO_2$ treated with calcium chloride solution

BLANK
PAGE

PHYSICOCHEMICAL STUDY OF LITHIUM PEROXIDE

T. V. Rode, T. A. Dobrynina and G. A. Golder

The possibility of the existence of a lithium peroxide was first suggested by Kralovanszky [1] in 1828. This author considered that when LiOH or Li_2CO_3 is heated in the air Li_2O_2 is formed. In 1857 Trost [2] passed dry oxygen over lithium heated to 200° and obtained a substance containing more oxygen than lithium oxide. This substance decolorized a solution of indigo in hydrochloric acid, was unstable to heat, and reacted at high temperature with gold, silver, and platinum. Trost [2] used iron crucibles in his work. De Forcrand [3] states that the combustion of lithium in oxygen yields only traces of lithium peroxide, since the latter is unstable at the combustion temperature of lithium and decomposes into lithium oxide and oxygen.

Attempts by other authors [4, 5] to prepare lithium peroxide at an oxygen pressure of 100 atm from lithium hydroxide [4] and from lithium oxide [5] at temperatures ranging from 875° to 570° were not successful. The attempts failed because the temperatures used were too high. In a previous paper [6] we have shown, and in the present investigation we have confirmed, that at atmospheric pressure decomposition of lithium peroxide occurs over the range 285-315°.

Another method for the preparation of alkali-metal peroxides, consisting in the oxidation of solutions of the metals in ammonia at low temperature, did not give satisfactory results in the case of lithium.

Pierron [7] studied the effects of concentration, temperature, and rate of passage of oxygen on the oxidation of a solution of lithium in liquid ammonia. A mixture of lithium oxide and lithium peroxide was always obtained, and the maximum yield of Li_2O_2 did not exceed 23%.

The principal method for the preparation of lithium peroxide consists in the oxidation of aqueous-alcoholic solutions of lithium hydroxide with hydrogen peroxide. This method was first proposed by de Forcrand. By the action of a large excess of H_2O_2 on an aqueous-alcoholic solution of lithium hydroxide, de Forcrand obtained the compound $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$, and after dehydration in a vacuum over phosphoric oxide at room temperature for 28 days this yielded almost anhydrous lithium peroxide ($Li_2O_2 \cdot 0.15H_2O$). Pierron [7] modified de Forcrand's method by raising the precipitation temperature to the boiling point and using 95% ethanol to dissolve the lithium hydroxide. The precipitate obtained was washed with boiling alcohol and vacuum-dried over phosphoric oxide, when it was found to have the composition $Li_2O_2 \cdot 0.01Li_2O$. Cohen [8] treated lithium ethoxide with hydrogen peroxide in an atmosphere of dry helium and obtained the compound $LiOOH \cdot H_2O$ (or $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$), which yielded anhydrous lithium peroxide after being vacuum-dried over phosphoric oxide for 18 days.

In the patent literature a number of methods are given for the preparation of lithium peroxide in presence of various organic substances that facilitate the dehydration of the products [9] or the oxidation of the alkali-metal ethoxide [10-13]. In 1951 Thompson and Kleinberg [14-15] studied the absorption spectrum of a preparation and showed that it is analogous to the absorption spectra of the higher peroxides of sodium and potassium. On the basis of these results the authors [14] postulate the existence of the higher peroxide of lithium LiO_2, stable at −78°.

The properties of lithium peroxide have received little study. In 1932 Blumenthal [16] investigated the thermal dissociation of Li_2O_2 by the dynamic method. According to this author's results, a dissociation pressure of 790 mm is already reached at 198°. We, however, have shown that Li_2O_2 begins to lose oxygen only at 285-315° [6]. According to Blumenthal's results [16], the heat of dissociation of Li_2O_2 to $Li_2O + \frac{1}{2}O_2$ is 13.6 kcal; the heat of formation of the peroxide from its elements is 144.8 kcal [17, 18]. In 1953 Rode and Dobrynina [6], working on the thermal analysis of lithium peroxide, established the existence of two modifications of lithium peroxide: α-Li_2O_2, stable up to 225°, and β-Li_2O_2, stable up to 300-315°, above which temperature the β-modification of lithium peroxide decomposes to the oxide. In the same work it was established that the lithium oxide formed by the decomposition does not react with stainless steel, but reacts with the glass of the vessel at 495°.

The crystal structure of lithium peroxide has been investigated by several authors [8, 9, 20, 21]. In the earliest X-ray investigations [8, 19, 20], Li_2O_2 crystals were assigned tetragonal symmetry with cell dimensions of $\underline{a}$ = 5.48 A, $\underline{c}$ = 7.74 A, and $\underline{a}/\underline{c}$ = 0.708 A. These values, however, led to considerable discrepancies between the measured and calculated values of the density ($\sigma_{meas.}$ = 2.297 g/cc, $\sigma_{calc.}$ = 2.56 g/cc) and the assignment of indices to the diffraction lines was found to be ambiguous. In a recent paper by Feher and coworkers [21], a hexagonal cell is assigned to lithium peroxide, its parameters being a = 6.305 A, c = 7.710 A, and a/c = 0.8197 A. From these cell dimensions and the measured density the authors calculated the number of atoms in the elementary cell to be z = 8. The calculated value of the density was σ = 2.48 g/cc. Optical investigations by these authors [21] showed the presence of an axis of symmetry of the sixth order in lithium peroxide crystals. Below, we give our results on the X-ray investigation of the α- and β-modifications of lithium peroxide; they confirm the results obtained by Feher and coworkers [21] for the α-modification.

EXPERIMENTAL

Experimental Procedure

We carried out a physicochemical study of the system consisting of lithium peroxide and lithium oxide, using various methods of physicochemical analysis: in addition to investigation of composition-temperature curves under dynamic conditions on a torsion balance and chemical and X-ray analysis of the starting materials, intermediate products, and final products formed by heat, we carried out a precise thermographic investigation coupled with parallel determinations of the amount of oxygen evolved. As a result of this complex study we obtained the composition-temperature diagram for the system Li_2O_2—Li_2O.

The thermograms were recorded on a Kurnakov photo-registering pyrometer, which is described in detail in a book by Berg, Nikolaev and Rode [22]. Heating was carried out in accordance with a straight-line law in a crucible furnace, which was connected to the mains through a voltage regulator. Heating was at the rate of 6° per minute. Two thermograms were recorded at a rate of 100° per minute by the method proposed by Berg and Rassonskaya [23]. Accuracy in the thermographic recording was attained by considerably reducing the amount taken, which was from 0.07 to 0.2 g.

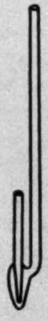


Fig. 1. Vessel for determining the thermogram with simultaneous measurement of evolved gas.

Thermograms were determined in silica test tubes, in stainless steel beakers, and also in Pyrex Stepanov vessels [22], which we modified slightly (see Fig. 1). In all experiments the test samples were taken in a chamber containing air freed from moisture and carbon dioxide by suitable absorbents (P_2O_5, Na_2O_2 and KO_2). The exit tubes of the Stepanov vessels were connected via a sulfuric acid absorber to a measuring buret, by means of which the kinetics of oxygen evolution could be followed during the recording of the thermogram, so that polytherms for the decomposition of the investigated samples could be obtained. The gas was brought to normal conditions, and a correction was made for its thermal expansion. In experiments carried out in Stepanov vessels, the specimens were again isolated from moisture and atmospheric carbon dioxide during the heating process.

In order to interpret the thermal effects observed on the thermograms, separate experiments were carried out in which specimens were heated to temperatures below and above those of the thermal effects. These specimens were investigated by X-ray and chemical analysis, and for control purposes their thermographs were determined. The chemical analysis was for active oxygen, which was determined from the volume of gas evolved in the catalytic decomposition of the specimens with cobalt sulfate solution.

For X-ray analysis the specimens were placed in Pyrex capillaries in the dry chamber referred to above. Copper radiation with a nickel filter was used in a RKU-114 camera. The spacing of the interference lines was measured with an IZA-2 comparator having a modified optical system, the magnification being about 4.

Composition-temperature range curves were determined under dynamic conditions from the loss in weight of the substance, which was measured on a torsion balance. Weighing was performed without removing the specimens from the vertical tube furnace, so as not to disturb the course of the heating of the substance. Readings were taken every minute. Heating was carried out both in an atmosphere of dry air and in a stream of dry oxygen, the rate of heating being 13, 5.5, and 1.5 degrees per minute. The lithium peroxide was synthesized by Dobrynina and had the following composition: lithium peroxide — 98.93%; total impurity (H_2O and H_2O_2) — 1.07%; CO_2 — none detected.

Thermographic Investigation

Fig. 2 shows the differential thermogram for lithium peroxide (Curve 1) and the simultaneous record (polytherm) of the amount of oxygen evolved during heating (Curve 2). Along the axis of abscissas time is plotted in minutes for both curves. The data for Curve 2 are given in Table 1.

The differential thermogram (Curve 1, Fig 2) shows the presence of the following thermal effects: at the beginning, at about 100°, there is scarcely appreciable inflection corresponding to the removal of loosely bound water: then, from 225° to 235°, there is a well-marked irreversible exothermic effect. Chemical analysis of a specimen heated — also in a Stepanov vessel — to 250°, i.e., above the temperature for the effect, showed that this effect is not accompanied by change in the composition of the substance. This can be seen also from Curve 2 (Fig. 2) for the evolution of oxygen, for in the section corresponding to this exothermic effect no evolution of gas has yet occurred. The irreversibility of this effect was established by an examination of the curves (not given here)

TABLE 1

Evolution of Gas During the Heating of Lithium Peroxide

Time (minutes)	Temperature (°C)	Volume of gas evolved (ml at STP)	Reading of differential galvanometer (scale divisions)	Time (minutes)	Temperature (°C)	Volume of gas evolved (ml at STP)	Reading of differential galvanometer (scale divisions)
0	18	0	0	47	342	33.5	−5.0
15	145	0	−0.5	48	—	41	−5.0
25	210	0.0	−0.7	49	—	47.2	−4.5
37	295	0.5	−0.7	50	367	50.2	−2.5
39	—	1.6	−0.8	51	375	51.4	−0.3
41	315	5.0	−1.3	58	—	51.4	+ 1.0
42	—	7.8	−1.5	65	437	52.4	+ 2.0
43	325	9	—	82	—	53.4	+ 4.7
44	—	11	−2.7	103	580	54.5	+ 4.5
45	—	18.5	−3.5	115	—	54.5	+ 4.0
46	—	26	−4.5	130	723	54.5	+ 4.5

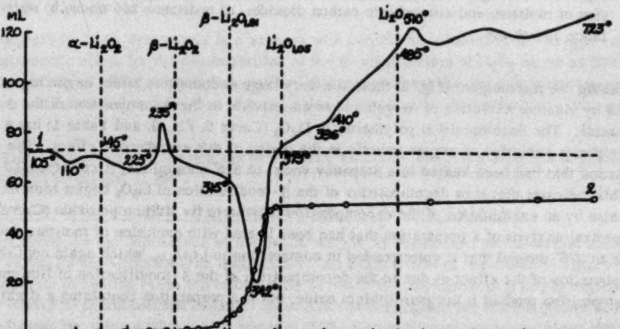


Fig. 2. Thermogram for lithium peroxide, with simultaneous record of the decomposition polytherm.

for the cooling of preparations heated to 250° and for the reheating of the same preparations. The irreversibility of the process and the constancy of composition gave reason to suppose that this exothermic effect is associated with a polymorphous transformation of lithium peroxide. As will be seen below, X-ray analysis confirmed the correctness of our supposition regarding the nature of this effect and the existence, therefore, of lithium peroxide in two modifications. The first of these, which is obtained under the usual conditions of synthesis and is stable up to 225°, we have called α-Li_2O_2 [6], and the second, which is formed as the result of changes occurring at 225° and is stable up to 285-315°, we have called β-Li_2O_2.

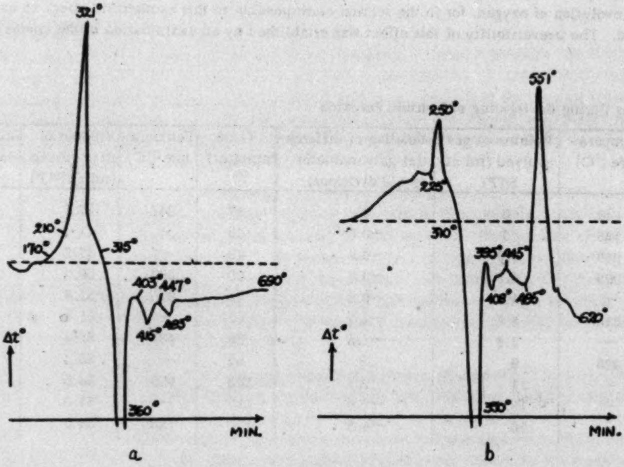


Fig. 3. Thermogram for lithium peroxide determined in a steel vessel without exclusion of moisture and atmospheric carbon dioxide: a) resistance 300 ohms; b) resistance 100 ohms*

Further along the thermogram (Fig. 2) there is a very large endothermic effect beginning at 315°, which is accompanied by vigorous evolution of oxygen and so corresponds to the decomposition of the β-modification of lithium peroxide. The decomposition polytherm for Li_2O_2 (Curve 2, Fig. 2, and Table 1) has a sharp rise associated with vigorous evolution of oxygen exactly in the region of this endothermic effect. The chemical analysis of a preparation that had been heated in a Stepanov vessel to 315° showed that it corresponded in composition to $Li_2O_{1.91}$. This indicates that slow decomposition of the β-modification of Li_2O_2 begins somewhat below 315°. This is shown also by an examination of the decomposition polytherm for lithium peroxide (Curve 2, Fig. 2, and Table 1). Chemical analysis of a preparation that had been heated with exclusion of moisture and atmospheric carbon dioxide to 375° showed that it corresponded in composition to $Li_2O_{1.05}$, which again confirms the correctness of our explanation of the effect as due to the decomposition of the β-modification of lithium peroxide. However, the decomposition product is not pure lithium oxide, but is a preparation containing a slight excess of active oxygen ($Li_2O_{1.05}$).

Finally, at 495-510° there is a small but clearly marked exothermic effect on the thermogram, which might possibly be explained by the crystallization of amorphous lithium oxide formed in the decomposition. However, the X-radiogram of a preparation obtained by treatment in absence of moisture and atmospheric carbon dioxide at 375°, i.e., immediately above the temperature of the decomposition effect, showed that lithium oxide is formed directly in the crystalline state (see below in the section on X-ray studies; see also Table 4). Further investigation showed that this exothermic effect corresponded to interaction with the glass of the vessel. In order to exclude the possibility of such interaction we determined the thermogram in a 0.5 ml stainless steel beaker, and the curve obtained is given in Fig. 3a. On this curve there are again some well-defined effects: an exothermic effect corresponding to the conversion of the α-modification of lithium peroxide into the β-modification, which begins here at 210°, and an endothermic effect corresponding to the decomposition of the β-modification of lithium peroxide, which begins at 315°. Beyond this point there is no exothermic effect to be found on the thermogram. The disappearance of the exothermic effect at 495-510° on the thermogram when Pyrex glass is replaced by stainless steel confirms that this exothermic effect corresponds with the interaction of lithium oxide formed by decomposition of the peroxide with the glass of the vessel. This is confirmed also by a thermogram determined in a quartz-glass test tube (Fig. 3b), the conditions then being such that the interaction of lithium oxide with the glass will be even greater. On this thermogram the exothermic effect for the interaction of the lithium oxide formed with silica, which begins at 495°, is even more marked than in the experiments in a Pyrex-glass vessel.

---

* This description of the curves does not appear to be correct. See text. [Publisher].

Kracek [24] has studied the phase diagram for the binary system lithium oxide—silica, and he established the existence of three intermediate compounds in this system: $2Li_2O \cdot SiO_2$, $Li_2O \cdot SiO_2$, and $Li_2O \cdot 2SiO_2$. Austin [25] gives X-ray data for all these three compounds. The chemical analysis of the preparation that we obtained in a quartz vessel heated to 658° and a comparison of its X-radiogram with the X-radiograms given by Austin [25] (see below, Table 5) completely confirm the results of thermographic and chemical analysis, namely, that the lithium oxide formed reacts with the glass of the vessel at about 500° with formation of lithium monosilicate $Li_2O \cdot SiO_2$ (Li_2SiO_3).

On the thermograms determined in steel beakers and quartz test tubes (Figs. 3a and 3b), i.e., under conditions such that the specimens were not isolated from the action of atmospheric moisture, we observed two additional small endothermic effects beginning at about 400° and at about 445°, respectively; these were due to the action of atmospheric moisture and the formation of a small amount of lithium hydroxide.

It is reported in the literature [17, 18] that lithium peroxide is not hygroscopic, but this is not true. Our observations have shown that, when allowed to stand in a desiccator over dilute (2%) sulfuric acid, both the α- and β-modifications of lithium peroxide avidly absorb moisture with formation of lithium hydroxide. Both of the additional effects referred to above — at 403-415° and at 445° — correspond to the presence of lithium hydroxide, which undergoes a polymorphous change when the first effect occurs, as established in the work of Khitrov, Khitrova and Khmelkov [26], and melts without decomposition when the second effect occurs.

The hypothesis that we advanced in a previous paper [6] regarding the cause of the first of these additional effects (at 403-415°)(removal of water in excess of that required by the formula LiOH) has not been confirmed. This effect is analogous to the effect given by sodium hydroxide and is to be explained by the occurrence of a polymorphous change of lithium oxide.

On a thermogram for Li_2O_2 determined in a vacuum with continuous removal of the oxygen evolved by pumping, the endothermic effect for the decomposition of the β-modification of Li_2O_2 began at 283°. The rate of heating, which also has an effect on the decomposition temperature, was the same in both cases, namely, 6 degrees per minute. It follows, therefore, that with reduction of pressure the decomposition temperature of β-Li_2O_2 falls.

On thermograms determined at 100 degrees per minute, which are not given here, the beginning of the endothermic decomposition effect was at 390°.

Curves for the Loss in Weight, Determined on a Torsion Balance

Fig. 4 shows curves for the dependence of the loss in weight, as determined with a torsion balance, on time, and Fig. 5 shows curves for its dependence on temperature. An examination of the curves in Figs. 4 and 5 shows that increase in the rate of heating raises the temperature at which decomposition of β-Li_2O_2 begins: at 13 degrees per minute (Curve 1) decomposition began at about 310°; at 5.5 degrees per minute (Curve 2) it began at 288°; and at 1.6 degrees per minute (Curve 3) it began at 282°. Comparison of the curves given in Fig. 5 shows that increase in the rate of heating displaces the whole of the curve for the loss of weight into the region of higher temperatures.

Two curves determined at 5.5 degrees per minute, one obtained by heating Li_2O_2 in an atmosphere of dry air, and the other obtained in a stream of dry oxygen, show that, as might be expected, the presence of oxygen somewhat retards the decomposition of lithium peroxide.

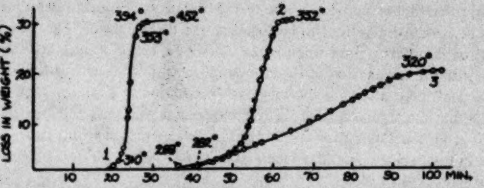


Fig. 4. Curve for the dependence of the loss in weight of lithium peroxide in an atmosphere of air on the rate of heating: 1) 13° per minute, 127 ohms; 2) 5.5° per minute, 100 ohms; 3) 1.6° per minute, 70 ohms.

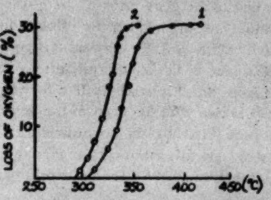


Fig. 5. Curve for the dependence of the loss in weight of lithium peroxide in at atmosphere of air on the rate of heating: 1) 13° per minute; 2) 5.5° per minute.

Results of an X-Ray Study of Preparations Obtained by Heating Lithium Peroxide

In recent work by Feher and coworkers [21] it was established that lithium peroxide synthesized in the usual way has hexagonal syngony with cell parameters of $\underline{a}$ = 6.305 A, $\underline{c}$ = 7.710 A, and $\underline{a}/\underline{c}$ = 0.8197 A. Table 2 gives our results on the interplanar spacing of the α-modification of lithium peroxide. The data of Feher and coworkers [21] is given in the same table for comparison, and they agree very well with ours. All of the observed lines can be assigned to indices of the hexagonal lattice. Our results, therefore, confirm those of Feher [21] and show that the α-modification has hexagonal syngony with the cell parameters given above; they conflict with the results of previous authors [8, 9, 20], which assign a tetragonal cell to this substance.

TABLE 2

Interplanar Spacing of α-Li_2O_2

No.	Our results		Feher's results		hkl
	I	d	I	d	
1	weak	3.84	medium	3.86	002
2	strong	2.74	mod. strong	2.74	020
3	v. strong	2.59	v. strong	2.59	021
4	mod. strong	2.23	medium	2.23	022
5	v. weak	1.90	v. weak	1.94	004
6	medium	1.87	medium	1.88	023
7	v. strong	1.58	strong	1.58	220
8	weak	1.45	weak	1.46	222
9	strong	1.34	mod. strong	1.34	223
10	weak	1.29	weak	1.29	042
11	weak	1.22	weak	1.21	043
12	medium	1.02	medium	1.02	045
13	medium	1.00	medium	0.993	226

TABLE 3

Interplanar Spacing of β-Li_2O_2

No.	I	d	No.	I	d
1	medium	4.35	6	weak	1.86
2	medium	3.08	7	medium	1.76
3	v. strong	2.75	8	strong	1.66
4	medium	2.52	9	medium	1.49
5	v. weak	1.94			

The β-modification of lithium peroxide, the existence of which had been established by the method of thermography, was synthesized in a separate experiment from the α-modification by heating it for six hours at 235° in a current of dry oxygen. Its interplanar spacing is given in Table 3. However, as the crystals of β-Li_2O_2 evidently belong to a lower syngony, it was not found possible to carry out the assignment of indices and the calculation of parameters.

It was established by thermography and simultaneous determination of decomposition polytherms that lithium peroxide decomposes at about 300-315° with formation of lithium oxide when the specimen is well-isolated from the action of atmospheric moisture and carbon dioxide. In view of the presence of an exothermic effect at 495° on the Li_2O_2 thermogram, the question arose of whether this was a crystallization effect of lithium oxide formed in the amorphous state. Hence, in a separate experiment a sample of Li_2O_2 was heated to 350° with careful exclusion of moisture and carbon dioxide. The X-radiogram of this sample showed that it consisted of crystalline lithium oxide. Its interplanar spacing is given in Table 4. Mensuration of the X-radiogram gave spacings in good agreement with those reported in the literature [27-29] for the cubic lattice of lithium oxide having the parameter $\underline{a}$ = 4.619 A.

TABLE 4

Interplanar Spacing of Li_2O

No.	I	d		hkl
		experimental	calculated	
1	v. strong	2.66	2.664	111
2	weak	2.30	2.305	200
3	v. strong	1.63	1.630	220
4	strong	1.40	1.400	311
5	medium	1.15	1.151	400
6	medium	1.06	1.058	331
7	strong	0.945	0.924	422
8	medium	0.890	0.888	511
9	medium	0.820	0.815	440
10	medium	0.781	0.780	531

TABLE 5

Interplanar Spacing of Preparation No. 10, Heated to 658° in a Quartz Stepanov Vessel

No.	Data for Preparation No. 10		Data of Austin for Li_2SiO_3 [25]	
	I	d	I	d
1	medium	4.71	v. strong	4.70
2	medium	3.98	medium	4.02
3	strong	3.36	medium	3.32
4	v. strong	2.74	v. strong	1.72
5	strong	2.37	medium	2.35
6	weak	1.79	weak	1.78
7	medium	1.65	weak	2.66
8	medium	1.58	medium	1.57

TABLE 6

Composition-Temperature Diagram for the System $Li_2O_2-Li_2O$ (under conditions of careful exclusion of atmospheric moisture and carbon dioxide)

No.	Temperature (°C)	Composition	X-ray data
1	20	α-Li_2O_2	Given in Table 5
2	200	α-Li_2O_2	Identical with preceding
3	215	α-Li_2O_2	Ditto
4	235	β-Li_2O_2	Given in Table 6
5	315	β-$Li_2O_{1.91}$*	
6	350	$Li_2O_{1.05}$	Given in Table 7
7	480	Li_2O	Identical with preceding
8	658 (heated in a quartz vessel)	Li_2SiO_3	Given in Table 8

---

* Observed displacement of interference lines is within limits of experimental error.

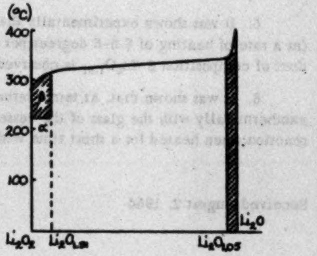


Fig. 6. Composition-temperature diagram for the system lithium peroxide–lithium oxide.

Table 5 gives the interplanar spacing of Preparation No. 10. This material was obtained as the result of the determination of a thermogram for temperatures up to 658° in a Stepanov vessel, which was completely destroyed by the end of the experiment. Comparison of the results obtained for this preparation with Austin's results [25], which are given in the same table, confirms the suggestion made above concerning the formation of lithium monosilicate Li_2SiO_3 by reaction of lithium oxide with the glass of the vessel at temperatures above 500°.

Composition-Temperature Diagram for the System $Li_2O_2-Li_2O$

We have also determined the composition-temperature diagram for the system $Li_2O_2-Li_2O$. Weighed samples of lithium peroxide were heated in Stepanov vessels at various temperatures (as indicated by the thermograms) for several hours. At the end of the treatment the loss in weight was determined and chemical and X-ray analyses were carried out on the products. A comparative examination of all of the results so obtained made it possible to construct the composition-temperature diagram of the lithium peroxide–lithium oxide system, and we give this in Fig. 6. The corresponding numerical data are given in Table 6.

The field of existence of the α-modification of lithium peroxide extends from room temperature to 225°, and it does not decompose at this temperature, but passes into the β-modification, which is stable up to 280°. Up to this temperature, no decomposition of the β-modification of lithium peroxide is observed in an atmosphere free from moisture and carbon dioxide. Between 280° and 315° very slow decomposition of β-Li_2O_2 sets in and proceeds until a product of composition $Li_2O_{1.91}$ is obtained. At 315° there is vigorous decomposition, but complete loss of active oxygen to give a product having the composition of lithium oxide is not observed, and the decomposition product corresponds to the formula $Li_2O_{1.05}$. Thus, between the compositions β-Li_2O_2 and β-$Li_2O_{1.91}$ and from $Li_2O_{1.05}$

to Li_2O, regions of phases of variable composition are observed, and between the compositions β-$Li_2O_{1.91}$ and $Li_2O_{1.86}$ there is a heterogeneous region.

SUMMARY

1. A physicochemical study was made of the system Li_2O_2—Li_2O with the application of various methods of physicochemical analysis. Composition-temperature curves were determined under dynamic conditions with a torsion balance, chemical and X-ray analyses were made on the original substances and the intermediate and final products formed during heating, and also a precision thermographic investigation was carried out with simultaneous determination of the amount of oxygen evolved.

2. On the basis of the results of this complex study we constructed the composition-temperature diagram for the system lithium peroxide—lithium oxide (Fig. 6).

3. It was established that in this system there is an irreversible polymorphous change at about 225° and that lithium peroxide occurs in two modifications: α-Li_2O_2, stable to 225°, and β-Li_2O_2, stable to 280-315°.

4. The results of Feher and coworkers [21] concerning the assignment of α-Li_2O_2 to the hexagonal syngony (and not the tetragonal, as considered previously) were confirmed. The interplanar spacings of the β-modification were reported.

5. It was shown experimentally that lithium peroxide decomposes endothermically over the range 315-345° (at a rate of heating of 5.5-6 degrees per minute). The beginning of slow decomposition with formation of a product of composition β-$Li_2O_{1.91}$ is observed already at 280-315°.

6. It was shown that, at temperatures of 495° and above, the lithium oxide formed by decomposition reacts exothermically with the glass of the vessel and yields lithium monosilicate. Lithium oxide does not undergo any reaction when heated for a short time with stainless steel at 690°.

Received August 2, 1954

N. S. Kurnakov Institute of General and Inorganic
Chemistry of the USSR Academy of Sciences

LITERATURE CITED

[1] Kralovanszky, Schw. J., 54, 346 (1828).

[2] L. Trost, Ann. chim. Phys. (3), 51, 103 (1857).

[3] R. de Forcrand, Comptes rend., 130, 1465 (1900).

[4] F. Fischer, H. Ploetze, Z. anorg. Chem., 75, 30 (1912).

[5] J. Milbauer, Chem. Z. 40, 587 (1916).

[6] T. V. Rode and T. A. Dobrynina, Proc. Acad. Sci. USSR, 91, 125 (1953).

[7] P. P. Pierron, Bull., 6, 235 (1939).

[8] A. Cohen, J. Am. Chem. Soc., 74, 3762 (1952).

[9] P. Winternitz, U. S. Patent 2,488,485, Nov. 15 (1949); Chem. Abs., 44, 1660 (1950).

[10] Farbenindustrie, Chem. Abs., 30, 8537 (1936); 32, 315 (1938).

[11] Mathieson Alkali Worke, French Patent 826,431, Mar. 31 (1938).

[12] G. Pfleiderer, U. S. Patent 2,215,856, Sept. 24 (1941); Chem. Abs., 35, 861 (1941).

[13] G. Cunningham, Ber., 703, 894, Feb. 13 (1941).

[14] J. Thompson, J. Kleinberg, J. Am. Chem. Soc., 73, 1243 (1951).

[15] J. Kleinberg, J. Chem. Education, 29, 325 (1952).

[16] M. Blumenthal, Roezniki chemji., 12, 119, 232 (1932); C. 1932, II, 2589.

[17] M. E. Pozin, Hydrogen Peroxide and Peroxy Compounds, State Chem. Press, 1951, p. 296.

[18] W. Machu, Das Wasserstoffperoxyd und Perverbindungen. 2. Aufl., Wien, 1951, S. 230.

[19] A. Aguzzi, F. Genoni, Gazz. chim. Ital., 68, 816 (1938).

[20] F. Feher, Angew. Chem., 51, 597 (1938).

[21] F. Fehr, I. Wilucki, G. Dost., Ber., 86, 1429 (1953).

[22] L. G. Berg, A. V. Nikolaev and E. Ya. Rode, Thermography, Acad. Sci. USSR Press, Moscow, 1944.

[23] L. G. Berg and I. S. Rassonskaya, Proc. Acad. Sci. USSR, 73, 113 (1950).

[24] F. Kracek, J. Phys. Chem., 34, (12), 2641 (1930).

[25] A. Austin, J. Am. Ceram. Soc., 30, 218 (1947).

[26] V. A. Khitrov, N. N. Khitrova and V. F. Khmelkov, J. Gen. Chem., 23, 1630 (1953) (T.p. 1707).*

[27] E. Zintl, A. Harder, B. Dauth, Z. Elektrochem., 40, 588 (1934).

[28] J. M. Bijvoet, A. Karssen, Rec. trav. chim., 43, 680 (1924).

[29] B. F. Ormont, Structure of Inorganic Substances, State Tech. Press, Moscow, 1950.

---

* T.p. = Consultants Bureau Translation pagination.

SYNTHESIS OF 2,2'-AZOBIS[2-METHYLPROPIONITRILE]

LABELED WITH RADIOACTIVE CARBON (C^{14})

M. M. Koton, T. M. Kiseleva and F. S. Florinsky

Free radicals are now extensively applied in the initiation of polymerization reactions, and for the detailed study of the mechanisms of such reactions initiators containing radioactive carbon in their molecules have been used [1]. Koton, Kiseleva and Bessonov [2] have synthesized benzoyl peroxide containing radioactive carbon (C^{14}) in the carbonyl group, and they showed that benzoyl peroxide breaks down into benzoate radicals which initiate the polymerization of styrene. In view of the extensive use of 2,2'-azobis[2-methylpropionitrile] as an initiator in radical polymerization, we have now carried out the synthesis of this compound labeled with radioactive carbon (C^{14}).

EXPERIMENTAL

Preparation of Radioactive Acetone $CH_3C^{14}OCH_3$

Acetic acid containing radioactive carbon in the carboxyl was prepared [3] for use in the synthesis of radioactive acetone:

$$BaC^{14}O_3 + 2HClO_4 \rightarrow Ba(ClO_4)_2 + H_2O + C^{14}O_2$$

$$CH_3MgI + C^{14}O_2 \rightarrow CH_3C^{14}OOMgI \xrightarrow{HOH} CH_3C^{14}OOH + Mg(OH)I$$

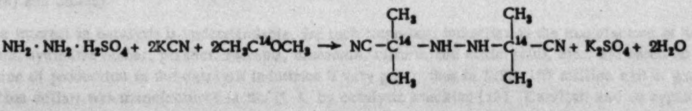
Carbon dioxide was prepared in a special apparatus from 0.25 g of active barium carbonate by the action of 5 ml of perchloric acid. The carbon dioxide was cooled, first with liquid nitrogen, and then with solid carbon dioxide, and 30 ml of 0.8 N ethereal methylmagnesium iodide was added. The reaction mixture was kept for one hour in an ice bath and then for one hour at room temperature for completion of the reaction. Decomposition was effected with 10% aqueous hydrochloric acid, and the ethereal solution was separated, washed, and dried. Ether was distilled off, 2 g of silver sulfate was added to the residue, and acetic acid was distilled over into a titrated solution of barium hydroxide. The resulting solution of barium acetate was evaporated to dryness in a platinum dish. The yield of barium acetate was 0.50 g (78.8%). It was subjected to pyrolysis at 500° [4]:

$$(CH_3C^{14}OO)_2Ba \rightarrow BaC^{14}O_3 + CH_3C^{14}OCH_3$$

and radioactive acetone was obtained in quantitative yield.

Preparation of Radioactive 2,2'-Hydrazobis[2-methylpropionitrile] [5]

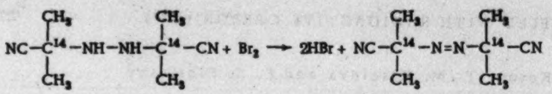
A solution of 12.15 g of hydrazine sulfate in 50 ml of water was warmed slightly, and concentrated potassium cyanide solution (12.15 g of KCN in 15 ml of water) and 10.85 g of radioactive acetone were added. The mixture was stirred vigorously until crystallization set in. After twelve hours the crystals were separated from the liquid, washed with water, and used in the next stage of the synthesis without further purification. The yield was 15.0 g.



$$NH_2\cdot NH_2\cdot H_2SO_4 + 2KCN + 2CH_3C^{14}OCH_3 \rightarrow NC-\overset{CH_3}{\underset{CH_3}{C^{14}}}-NH-NH-\overset{CH_3}{\underset{CH_3}{C^{14}}}-CN + K_2SO_4 + 2H_2O$$

Preparation of Radioactive 2,2'-Azobis[2-methylpropionitrile]

The 2,2'-hydrazobis[2-methylpropionitrile] prepared as above (15.0 g) was dissolved in 50 ml of ethanol, the solution obtained was warmed slightly, and a solution of 15 ml of concentrated hydrochloric acid in 30 ml of water was added. The solution was cooled with ice and salt, and it was then stirred vigorously while a solution of 4 g of bromine in 415 ml of water was added slowly. The end of the oxidation process was indicated by permanent coloration of the solution. A white crystalline precipitate formed; it was separated, washed with water, and recrystallized from ether or ethanol.



$$NC-\overset{CH_3}{\underset{CH_3}{C^{14}}}-NH-NH-\overset{CH_3}{\underset{CH_3}{C^{14}}}-CN + Br_2 \rightarrow 2HBr + NC-\overset{CH_3}{\underset{CH_3}{C^{14}}}-N=N-\overset{CH_3}{\underset{CH_3}{C^{14}}}-CN$$

The yield was 6.6 g of substance in the form of fine white crystals, melting with decomposition at 100-103°.

Found %: N 34.05

$C_8H_{12}N_4$. Calculated %: N 34.14

According to the results obtained in S. E. Bresler's laboratory, the specific activity of the preparation obtained was 30 microcuries per gram.

SUMMARY

The synthesis is described of 2,2'-azobis[2-methylpropionitrile] labeled with radioactive carbon.

Received December 20, 1954

Institute of Macromolecular Compounds of the USSR Academy of Sciences

LITERATURE CITED

[1] R. Colclough, J. Pol. Sci., 8, 467 (1952); L. Arnett, I. Peterson, J. Am. Chem. Soc., 74, 2031 (1952).

[2] M. M. Koton, T. M. Kiseleva, and M. I. Bessonov, Proc. Acad. Sci. USSR, 95, 85 (1954).

[3] I. Bruggen, C. Claycomb, T. Hutchens, Nucleonics, 7, 45 (1950).

[4] M. Calvin, Isotopic Carbon, 1949, N.Y.

[5] I. Thiele, K. Heuser, Ann., 290, 1 (1896).

PRESENT STATE OF THE CATALYSIS PROBLEM AND THE THEORETICAL BASIS OF THE SEARCH FOR CATALYSTS

A. A. Balandin

(Paper read at a general meeting of the Division of Chemical Sciences
of the Academy of Sciences of the USSR, March 31, 1955)

In 1954 there was much activity in the field of catalysis. New monographs on catalysis appeared (Boreskov [1], Emmett [2], Advances in Catalysis [3], a section in a book by Semenov [4]). In April there was a conference in Moscow on the electronic properties of catalysts, and at this conference important communications were made relating to experimental support for the electronic theory of catalysis (S. Z. Roginsky, F. F. Volkenshtein) the desorption of molecules under the action of light was described (A. N. Terenin).

In June there was an international conference in Paris on the structure and texture of catalysts [5]. The Soviet delegation was headed by B. A. Kazansky, and papers were read at the conference by G. M. Panchenkov and L. A. Nikolaev. The conference again showed the necessity for the application of modern methods in the study of solid catalysts, namely, X-ray-structure, electronographic, electron-microscopic, magnetic, adsorption, thermographic, calorimetric, and other methods. Several papers were devoted to the electronic theory of catalysis.

In October there was an All-Union conference in Alma Ata on hydrogenation and oxidation (president of organizing committee D. V. Sokolsky) [6]. At the end of October, under the initiative of A. V. Topchiev, a conference was called in Moscow on the complex chemical treatment of natural and industrial petroleum gases, and about one-half of the papers were devoted to applied catalysis. The work of the Moscow Inter-Institute Seminar on Catalysis was renewed.

In 1954 a group of scientists with the cooperation of the most eminent specialists on catalysis in the country worked out a plan for tackling the problem of the "scientific basis of the selection of catalysts", which was listed by the Presidium of the Academy of Sciences of the USSR among problems of particular importance [7]. In connection with the development of the plan, a conference was held in Moscow University, and not only Moscow scientists, but also scientists from Leningrad, the Ukraine, White Russia and the Caucasus took part. An important result of the work done was the isolation of the central problem in catalysis — the selection of catalysts. Other valuable results were the experiment of combining the efforts of various schools of catalysis, the realization that the theory of catalysis in its present state is able to indicate what experimental data are required for the solution of the problem, and the support given to this undertaking by industry. The development of the theory of catalyst selection on the basis of material relating to practically important reactions should result in knowledge enabling us to direct and control these reactions better. Investigations on the problem of the scientific basis of the selection of catalysts have been included in the plans of several institutes, and they have already been started; a scientific council has been organized to deal with this problem, and it has begun work.

During 1954, important results on inorganic and organic catalysis were published. Of the latter the following should be noted: the formation of hydrocarbons having five-membered rings (Kazansky and Liberman [8], Shuikin [9]), hydrogenation (Ponomarev [10], Freidlin [11], Sokolsky [12]), alkylation (Turova-Polyak [13]), isomerization (Levina [14]), reactions of heterocycles (Yuryev [15], Sultanov [16], Kozlov [17]), mechanism of dehydration (Topchieva [18] and others).

The interest in catalysis is understandable, for such important industries as the manufacture of high-quality motor fuels, synthetic rubber, plastics, solvents, ammonia, sulfuric and nitric acids, etc., are based on catalysis. The volume of production in the catalysis industries is very great; thus in 1953, 137 million tons of gasoline valued at 22 billion dollars was manufactured in the U. S. by catalytic cracking [19]. Catalysis and its application are developing rapidly. There can be no doubt that in the future a considerable part of the material requirements of mankind will be satisfied with the aid of the catalytic treatment of coal, petroleum, gases, water and air.

The selection of catalysts has generally been carried out in an empirical fashion. This method is a very slow one; for example, it has now become known that in Germany 20,000 substances were tried as catalysts for the synthesis of ammonia. In foreign countries there are several institutes and large laboratories which work on the selection of catalysts.

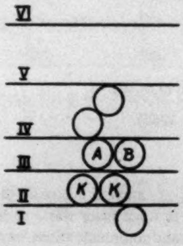


Fig. 1. Layers: I) carrier and foreign materials; II) active centers; III) reacting atoms; IV) substituents attached to them; V) molecular-adsorption layer; VI) diffusion layer.

It is necessary to find rational, nonempirical methods for the selection of catalysts. There are various schools and trends in the theory of catalysis: the deformation theory (Zelinsky [20], Bodenstein [21]); the theory of intermediate compounds (Sabatier [22]) and its modern variant, the theory of intermediate chemisorption (Rideal [23], Boreskov [24]); the multiplet theory (Balandin [25]); the theory of nonhomogeneity of surface (Taylor [26], Temkin [27], Roginsky [28]); the theory of assemblages (Kobozev [29]); the theory of supersaturation (Roginsky [30]); the electron-chemical theory (Riginsky and Volkenshtein [31]); the radical-chain theory (Semenov and Voevodsky [4]); the theory of absolute reaction rates (Temkin [32], Eyring [33]). Recently, a drawing together of different points of view is to be noted and several general principles have been elucidated which form the general outline of a unified theory of catalysis based on the theory of the structure of matter. It has been found that different theories often refer to different aspects of the phenomenon and are mutually complementary. This is particularly clear when considered in relation to the ideas developed by the present author [34] concerning the layered structure of the catalytic active complex (Fig. 1). The theories enumerated above relate mainly to layers II and III, whereas the work on hydrogenation by S. V. Lebedev, for example, relates to layer IV, and many of the investigations of S. Yu. Elovich on hydrogenation relate to layer VI.

We shall now examine the contributions made to the development of the problem of the selection of catalysts by the authors of theories relating to this problem. The chemical theory of intermediate compounds is able to explain the selectivity of catalysis by the selectivity of the affinity of catalysts; it was the first to establish the existence of a correspondence between reactions and catalysts. Its main defects are that it does not explain the causes of catalysis, but only indicates the way in which it arises, and that it has nothing to say about the effect of the conditions under which the catalyst is formed.

The electron-chemical theory is concerned with the electron levels of solid catalysts and molecules, the electron-donating and electron-accepting properties of molecules, the extent to which the Brillouen zones are filled, and the equilibrium of "holes"; it divides catalytic reactions into oxidation-reduction, with electron transfer, and acid-base, with proton transfer. Each of these classes has its own catalysts. The theory is strengthened by its power to deal with promotors, for the action of which it envisages a parallelism with their action on the conductivity of semiconductors, and also with variations associated with the mode and conditions of formation of the catalyst. It is essential that this progressive theory should be developed into a more concrete form.

The multiplet theory of catalysis occupies a central position, in the sense that there are possible transitions linking it with all of the theories referred to above. The multiplet theory distinguishes reacting, index groups of atoms in the molecules, and these become applied to atoms of the catalyst lattice, being attracted to the latter by chemical forces. A consideration of actual configurations and interatomic distances leads to the discovery of the existence of structural correspondence, which enables catalysts to be selected in accordance with their structures. In this way possible catalysts for the dehydrogenation of six-membered cycles were indicated and, in particular, the catalytic activity of rhenium for the dehydrogenation of cyclohexane was predicted. A consideration of the energies of bonds within the molecules and of bonds formed with the catalyst yields energy correlations which explain selectivity.

A very complete review of the structural aspects of the multiplet theory has been given recently by Trapnell [35]. We shall enumerate the new facts that form the basis of the proof of the correctness of the multiplet sextet model for the dehydrogenation of cyclohexane hydrocarbons and the hydrogenation of benzene in presence of metals. The proof is concerned with the view that the active face (111) of a face-centered lattice, the face (1000) of a hexagonal lattice, and also the ring lie flat on the surface of the catalyst.

1. Investigation of Pt, Pd, Ni, Fe, Cu and Ag alloys showed that as their compositions were changed their catalytic activity was retained so long as the structure required by the theory was retained. These results, which were obtained by Long, Frazer and Ott [36] and by Emmett and Skau [37] in 1953, were confirmed in an extensive and careful investigation by Rienäcker and Unger [38].

2. Rubinshtein, Minachev, and Shuikin [39] showed that as the Pt content of platinized charcoal was reduced the rate of hydrogenation of benzene changed symbatically with the reduction of the intensity of X-ray reflections from the face (111). Reflections from these faces disappear later than those from the others, and the catalytic activity disappears at the same time.

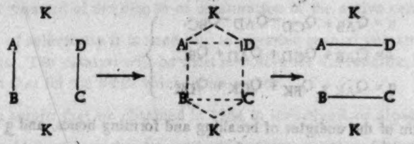
3. For a long time Beeck and others [40] considered that finely divided nickel owes its activity in hydrogenation to its (110) faces, since these faces are found on the electron-diffraction diagrams. In 1954 Sachtler, Dorgelo, and van der Knaap [41] showed by electron-microscope and electron-diffraction methods that the (110) face of the nickel lattice is oriented parallel to the substrate, but, owing to the rapid growth of (110) faces, only (111) and (100) faces remain on the surface exposed to the gas phase, so that these faces must be catalytically active in the given reactions. This is in accord with the multiplet theory.

4. According to Schuit and de Boer [42], consideration of the area occupied by hydrogen in adsorption experiments indicates that the (111) and (1000) faces of nickel are active in hydrogenation.

5. As Isagulyants has shown in our laboratory [43], cyclohexane and decahydronaphthalene are dehydrogenated with equal activation energies on platinum, and the same is true on Cr_2O_3. However, over platinum the reaction rates are different for the two compounds, whereas they are the same over Cr_2O_3. This indicates a flat disposition of the cycles on platinum and an edgewise disposition on Cr_2O_3.

6. From the measured entropy of adsorption and from the number of degrees of freedom derived from this, Kemball [44] found that benzene is adsorbed on the surface of metals such as mercury so that the plane of the ring is parallel to the metal surface.

We shall now consider doublet reactions of the type



(1)

Here the bonds A—B and C—D in the original molecules are broken and the bonds A—D and B—C are formed in the reaction products. This proceeds via the formation of an intermediate catalytic complex in which the original bonds are weakened and deformed on account of the attraction to the catalyst K; and already the formation of the bonds of the reaction products is beginning. As a limiting case of the deformation of bonds we have their complete rupture with formation of radicals attached to the surface.

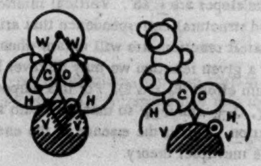


Fig. 2. Model of the catalytic dehydrogenation of alcohols, top and side views. Successive stages: a) $RHCHOH + V_2W_2 = RHCHOV + HW + VW$; b) $RHCHOV + VW = RHCVOV + HW$; c) $RHCVOV + 2HW = RHCO + H_2 + V_2W_2$ (V and W are catalyst valencies).

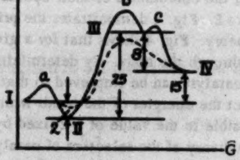


Fig. 3. Profile of potential surface for the dehydrogenation of alcohols. a, b and c denote the stages in Fig. 2. Heat changes are given in kcal/mole.

The scheme (1) implies a definite structural model, which is represented to scale for the dehydrogenation of alcohols [45] in Fig. 2. In the group CHOH, which lies on the surface, one H atom is first torn away with formation of a semihydrogenated form. The highest energy barrier is associated with the removal of the second H atom (see the broken line in Fig. 3).

The energetics of the scheme (1) and of the model in Fig. 2 are represented in Fig. 3, in which the energy level of the system is plotted to scale as ordinate, and the coordinate of the reaction is the abscissa. Denoting the energy of the bond X−Y for scheme (1) by Q_{XY}, we have:

$$\begin{aligned} E' &= -Q_{AB}-Q_{CD}+Q_{AK}+Q_{BK}+Q_{CK}+Q_{DK}; \\ E'' &= Q_{AD}+Q_{BC}-Q_{AK}-Q_{BK}-Q_{CK}-Q_{DK}. \end{aligned} \qquad (2)$$

In these multiplet-theory equations, E' is the energy for the formation of the multiplet complex and E" is the energy for its breakdown to form the reaction products. E' and E" correspond to the heights of the energy barriers of the reaction, and the rate of the reaction is determined by the more negative of them, E. The equations express the limiting case of the breakdown into atoms or free radicals. Actually, complete breakdown does not generally occur, but only deformation, so that for the activation energy we have

$$\epsilon \approx -\frac{3}{4}E. \qquad (3)$$

Equation 2 enables us to calculate the sequence in which the different bonds react. Such calculations have been made in cases in which the bonds with the catalyst Q_{AK}, etc., are known, namely, for Ni, for which the calculated sequence was in accord with experiment in almost all of the reactions studied (several hundred) [47, 48], and also for carbon [49, 50].

Equation 2 is of interest from the point of view of the theory of the selection of catalysts [46]. Let us introduce the quantities

$$\left.\begin{aligned} u &= Q_{AB}+Q_{CD}-Q_{AD}-Q_{BC}, \\ s &= Q_{AB}+Q_{CD}+Q_{AD}+Q_{BC}, \\ q &= Q_{AK}+Q_{BK}+Q_{CK}+Q_{DK}. \end{aligned}\right\} \qquad (4)$$

(u is the heat of reaction, s is the sum of the energies of breaking and forming bonds, and q is the adsorption potential of the catalyst). Equation (2) can now be rewritten in the form

$$\left.\begin{aligned} E' &= q-s/2+u/2, \\ E'' &= -q+s/2+u/2. \end{aligned}\right\} \qquad (5)$$

Equation 5 is represented graphically by pairs of straight lines forming "volcanolike" curves, as shown, for example, in Fig. 4, in which E is plotted as a function of q. The curves are determined only by the nature of the reaction, for the coordinates of their apexes are u/2 and s/2 and the slopes are ± 45°. Vertical intersecting lines correspond to E. Fig. 4 demonstrates the principles of energetic and structural correspondence that arise from the multiplet theory. Fig. 4 shows that for a given mechanism the greatest reaction rate will obtain when the vertical line passes through the apex. By determining E experimentally for a given reaction we may discover how much further the catalyst can be improved so that it may have its optimum effect ($E_{\phi} = u/2$). For this purpose it is necessary to select the energies of the bonds with the catalyst Q_{AK}, Q_{BK}, Q_{CK} and Q_{DK} so that their sum shall be as close as possible to the value of s/2 fixed by the nature of the reaction. This is the essence of the energetic aspects of the theory of the selection of catalysts, as derived from the multiplet theory.

This part of the theory is reminiscent of the theory of color: the index group corresponds to the chromophore group, and substituents in the molecule and catalyst atoms near to the active center correspond to bathochromic and hypsochromic groups. The position of the maximum of the volcanolike curve along the axis of adsorption potentials corresponds to the position of the center of the absorption band in the spectrum. It will be clear from the above considerations that for the purposes of the theoretical selection of catalysts it is essential that experimental material should be accumulated on bond energies, particularly individual, rather than mean values.

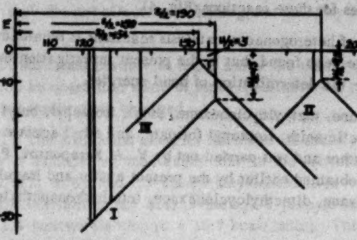


Fig. 4. Volcanolike curves: I) dehydrogenation of hydrocarbons: II) dehydrogeantion of alcohols; III) dehydration of alcohols. The vertical intersects correspond to experimental values of E for Cr_2O_3.

It must be remembered that the energy of the bond with the catalyst consists, in its turn, of two components expressing 1) the energy of the bond within the crystal, and 2) the effect of surrounding atoms on it. The first quantity can be found from thermochemical tables. The sum of all the energies of the bonds of the atoms A, B, C, and D with the catalyst is the normal adsorption potential q_s.

The second quantity is associated with the position of the active center on the nonhomogeneous surface, i.e., the number and arrangement of neighboring atoms in the lattice: the presence of foreign atoms also affects it. Summing these quantities for all atoms of the active center, we obtain the quantity λ, the sublimation term; thus

$$q = q_s + \lambda. \tag{6}$$

This fundamental equation resolves the dispute of whether the activity of a catalyst depends on its chemical nature (G. K. Boreskov) or on the way in which it is prepared and the presence of foreign substances (as S. Z. Roginsky thought at one time). The first of these views takes only q_s into account, and the second only λ; it is necessary to take both quantities into account.

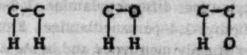
It should be noted also that the method of calculation by means of Equations 2-5 is very simple mathematically and will be familiar to chemists, who calculate molecular refractions, etc., by a similar additive method. Continuing this analogy, we may state that the quantity λ in Equation 6 is analogous to the increments for multiple bonds. Here λ is a measure of the degree of unsaturation of the active centers [51, 52].

In considerations of selectivity it is necessary to examine several volcanolike curves, according to the number of possible reactions. The catalyst will be most selective for the reaction having an absolute value of E that is appreciably less than that for the other volcanolike curves.

Let us pass to the results that we obtained in 1954 in investigations along the lines that we have indicated.

We shall first consider work on the determination of the energies of bonds formed with the catalyst, which was carried out by the kinetic method. This method was proposed by the present author [46], and it consists in the experimental determination of the activation energies of several reactions selected in such a way that the number of equations for E shall be equal to the number of unknowns (Q_{AK}, etc.).

Thus, this condition is satisfied by the reactions of dehydrogenation of hydrocarbons, dehydrogenation of alcohols, and dehydration of alcohols, the index groups being:



$$\begin{array}{ccc} \begin{array}{cc} C-&C \\ | & | \\ H & H \end{array} & \begin{array}{cc} C-&O \\ | & | \\ H & H \end{array} & \begin{array}{cc} C-&C \\ | & | \\ H & O \end{array} \end{array} \tag{7}$$

These types of reactions, and also certain others, have been investigated in our laboratory. For the scheme (7) the first of Equations 2 is transformed into the following:

$$\left.\begin{aligned} E_1' &= -2Q_{CH} + Q_{CK} + 2Q_{HK}, \\ E_2' &= -Q_{CH} - Q_{OH} + Q_{CK} + 2Q_{HK} + Q_{OK}, \\ E_3' &= -Q_{CH} - Q_{OH} + 2Q_{CK} + Q_{HK} + Q_{OK}. \end{aligned}\right\} \tag{8}$$

By determining ε experimentally and applying Equation 3, we find E_1', E_2', and E_3' and the separate energies of the bonds of the atoms C, H and O with the catalyst (Q_{CK}, Q_{HK}, and Q_{OK}), the values of Q_{CH} and Q_{OH} being known [47].

The results are given in Table 1.

It was found possible to construct the volcanolike curves for these reactions (Fig. 4).

It may be pointed out that the problem of the kinetics of heterogeneous-catalysis reactions is regarded as solved when the action constants and activation energies have been found, but in the present investigation the kinetics provide the solution of a problem of a higher order — the determination of bond energies.

The following substances were investigated: cyclohexane, methylcyclohexane, ethyl, isopropyl, butyl and isopentyl alcohols, 2-heptanol, cyclohexanol, formic and acetic acids, isopropyl formate, and ethyl acetate (the work was directed by A. A. Tolstopyatova and the present author and was carried out by V. A. Ferapontov, P. Teteni, I. R. Konenko and F. I. Kobos). Also, use was made of data obtained earlier by the present author and Isagulyants [43] for the dehydrogenation of cyclohexane, methylcyclohexane, dimethylcyclohexane, tetrahydronaphthalene, and tetrahydro-2-methylnaphthalene, these data being supplemented by A. A. Tolstopyatova, who investigated the catalysis of alcohols over the same catalyst. Further, in conjunction with N. A. Vasyunina, an investigation was made into the catalysis of amines, namely, 1-methylhexylamine, diisopropylamine, 1,3-dimethylbutylamine, 1,2,2-trimethylpropylamine, α-ethylbenzylamine, N^1,N^1-diethyl-1,4-pentanediamine. From these data together with the data on the catalysis of hydrocarbons by the authors already mentioned and by A. A. Tolstopyatova we succeeded in calculating the energy of the bond formed by nitrogen with the catalyst.

TABLE 1

Energies of Bonds with Catalyst. Results of Kinetic Determinations

Catalyst	Method of preparation	Q_{HK}	Q_{CK}	Q_{OK}	Substances
TiO_2	On asbestos as ready-made oxide	57.9	5.1	66.5	C_6H_{12}; C_2H_5OH
TiO_2	From $TiCl_4$	54.5	11.6	62.7	C_6H_{12}; C_2H_5OH
ZrO_2	From nitrate, precipitated with ammonia	54.5	4.1	53.5	C_6H_{12}; i-C_3H_7OH
ThO_2	From nitrate, precipitated with ammonia	66.7	5.8	50.4	$CH_3C_6H_{11}$; i-C_3H_7OH
ThO_2	On asbestos	62.7	6.0	45.0	$CH_3C_6H_{11}$; i-C_3H_7OH
Cr_2O_3	Precipitated with sodium carbonate	56.3	6.0	69.5	$CH_3C_6H_{11}$; i-C_3H_7OH
Cr_2O_3	Precipitated with ammonia	58.1	14.1	51.7	$CH_3C_6H_{11}$; i-C_3H_7OH
Cr_2O_3	On asbestos, precipitated with sodium carbonate.	62.1	6.8	43.0	$CH_3C_6H_{11}$; i-C_3H_7OH
Cr_2O_3	On asbestos, from ammonium dichromate	59.1	9.8	33.1	$CH_3C_6H_{11}$; i-C_3H_7OH
		58.2	4.7	49.7	C_6H_{12}; i-C_3H_7OH; HCOOH
Mo_2O_5	On asbestos	44.7	18.2	63.5	C_6H_{12}; i-C_3H_7OH; HCOOH
W_2O_5	On asbestos	48.5	16.3	53.3	$CH_3C_6H_{11}$; i-C_3H_7OH
WS_2		60.5	16.4	51.3	$CH_3C_6H_{11}$; i-C_3H_7OH
Ni		53	7	59	Thermochemical determination
		Q_{HK}	Q_{CK}	Q_{NK}	
ThO_2	From nitrate, precipitated with ammonia	53.3	18.6	21.0	1,2,2-Trimethylpropylamine
Th_2O	From nitrate, precipitated with ammonia	53.9	19.3	37.7	α-Ethylbenzylamine

As catalysts we took oxides of metals of the even groups of Mendeleev's system [54]:

From Group II: Be, Mg, Ca, Sr, Ba, Zn, Cd.

From Group IV: Ti, Zr, Th.

From Group VI: Cr, Mo, W.

Preparations of WS_2 and of Ni on Al_2O_3 were also investigated. The percentage conversions were determined experimentally under identical conditions, the extent to which reaction occurred being small. From these results, Arrhenius straight lines were constructed which gave a good fit to the experimental points. Diffusion did not play any part, the truth of this statement being verified in selected cases, in which it was shown that the grain size of the catalyst had no effect on the reaction rate.

The oxides of elements of Group II were found to be unsuitable for such investigations, since, although they effected the dehydrogenation and dehydration of alcohols (in the present investigation ϵ was measured in these cases), they did not effect the dehydrogenation of hydrocarbons, in spite of indications to the contrary in the literature [55].

It was found possible to make use of the results on the reactions over oxides of Group IV and Group VI metals (it should be noted that some of these reactions were effected for the first time over these particular catalysts). The following results were obtained.

1. The activation energies for identical index groups having different substituents were found to be identical. By way of example we may quote data for the dehydrogenation over Cr_2O_3 of cyclohexane (ϵ = 28.5), methylcyclohexane (ϵ = 26.6), and 1,3-dimethylcyclohexane (ϵ = 24.8), and also for the dehydrogenation over Ni on Al_2O_3 of 1-methylhexylamine (ϵ= 9.4), 3-methyl-1-propylbutylamine (ϵ = 9.6), diisopropylamine (ϵ = 8.6), and N^1,N^1-diethyl-1,4-pentanediamine (ϵ = 10.7 kcal/mole). This indicates, in agreement with theory, that the molecules are oriented identically on the catalyst.

2. Calculation yields values of Q_{EK} (by Q_{EK}, here and below, we understand the quantities Q_{AK}, etc.) of the expected order of magnitude.

3. For a given index the substituents have usually little effect on Q_{EK}. There is a scatter in the values for different catalysts, and also for different methods of preparing the catalysts, which is a reflection of the effect of λ. As indicated by Equation 6, this is in accord with theory.

4. The values found from the kinetics for Q_{HK} and Q_{CK} are often close to the thermochemical values, for example [56] Q_{HCr} = 56.3 (kinetic), Q_{HNi} = 53 (thermochemical); Q_{CCr} = 6.0 (kinetic), Q_{CCr} = 7 (thermochemical). The value of Q_{HK} varies only little in the reactions investigated. In one case a very much lower value, Q_{HK} = 44.7, was observed, from which it follows that the constancy is real and is not a mathematical artifact. Q_{CK} is a small quantity, and owing to its smallness the mode of formation of the catalyst has a great effect on its value; it sometimes suffers a twofold variation.

The fact that the oxides of elements of Group II do not promote the dehydrogenation of hydrocarbons, but bring about the catalysis of alcohols is probably to be explained as follows. Here Q_{HK} and Q_{CK} are small and are unable to bring about the lowering of E that is necessary for the dehydrogenation of hydrocarbons. Q_{OK}, on the contrary, is great, which is a deciding factor for the possibility of the dehydrogenation and dehydration of alcohols. This view is confirmed by the well-known fact that Group II metals have a high affinity for oxygen.

5. The bond O–K is found to be much more sensitive to various influences, so that Q_{OK} is much less constant. As will be seen from Table 1, Q_{OH} depends a) on neighboring atoms (the method of preparation) and substituents, and b) on the position of the element in Mendeleev's system.

6. The sequence of changes in Q_{OH} in a column of Mendeleev's stable does not correspond to the sequence of Q_{OK}, determined kinetically (see Table 1) and thermochemically, for we have:

$$\text{Ti–O} \ldots 84.0;\ \text{Zr–O} \ldots 94.0;\ \text{Hf–O} \ldots 97.4;\ \text{Th–O} \ldots 102.8.$$

It is probable that this noncorrespondence is to be explained by screening with other O atoms. In the approach of an oxygen atom from a molecule to a metal atom of small radius there is repulsion effect due to neighboring oxygen atoms in the lattice. This explanation is confirmed by thermochemical data, which show that as oxygen atoms accumulate in an oxide the mean bond energy falls; thus, the mean Q_{OCr} for Cr_2O_3 is 79, whereas for CrO_3 it is 53.

7. For the dehydrogenation and deamination of amines over ThO_2 (see Table 1) Q_{HK} and Q_{CK} were found to be close to the corresponding quantities for alcohols. The energy for the bond with the catalyst Q_{NK} was found to fall regularly between the values for C and O:

$$Q_{CK} < Q_{NK} < Q_{OK}.$$

The energy of the bond N–K is greatly affected by substitution in the molecule: when the substituent is aromatic Q_{NK} = 37.7, and when it is aliphatic Q_{NK} = 21.0. In its sensitivity to such effects the bond N–K is analogous to the bond O–K.

In such a new field as that which we are now considering there are naturally many problems that have not yet been investigated. As a result it was necessary to make several simplifying assumptions in the preceding calculations, and we shall now pass to a consideration of these assumptions.

1. The mechanism of both dehydrogenation and dehydration is assumed to be atomic, and not ionic. For dehydrogenation no doubts can arise, and we consider that convincing evidence for the atomic mechanism of dehydration is provided by a comparison of the regularities revealed by the work of Neiman and Shapavalov [57] on the one hand and of Bork [58] on the other (see Table 2). Experiments on the exchange of alkyl halides with bromine and iodine showed that with increase in the extent of substitution the rate constant k falls and the activation energy rises in ionic reactions, whereas the reverse is true in atomic reactions. In the dehydration of alcohols over Al_2O_3 the constants change with increase in the extent of substitution in the direction required by the atomic mechanism, thus confirming that the reaction occurs by this mechanism. By this we do not wish to imply that the ionic mechanism does not occur in presence of acidic catalysts, such as phosphoric acid on charcoal, or of aluminosilicates; on the contrary, the ionic mechanism does occur in these cases (cf. [59]). In this we are at variance with opinions, e.g. those of Dowden[60], which assert that dehydration is always an ionic reaction.

TABLE 2

Comparison of Atomic and Ionic Reaction Mechanisms

Reacting substance	Atom exchange (% per hour)		Ion exchange k	Ion exchange ε	Literature reference
CH_3I	0.03		1,200	15,400	[57]
$CH_2(CH_3)I$	0.05		65	19,000	[57]
$CH(CH_3)_2I$	1.4		10	20,500	[57]
	$k_{350°}$	ε			
CH_3CH_2OH	28.4	20,210			[58]
$CH_3CH_2CH_2OH$	55.4	18,330			[58]
$(CH_3)_2CHCH_2OH$	52.7	16,450			[58]

2. The dehydration of alcohols proceeds, as Topchieva and coworkers have shown [19], via a surface alkoxide. We assume that the role of the alkoxide in dehydration is analogous to that of the semihydrogenated form in dehydrogenation. As shown above, the existence of a semihydrogenated form finds its place in the scheme of calculation adopted, and the same is true of the alkoxide.

3. The reactions under comparison should be carried out at the same active centers. However, if the differences in the latter are not great, then they have little effect in the results in view of the form of the equations for determining Q_{EK}.

4. The rate of reaction should rise with decrease in ε. The experimental results show that we are indeed dealing here with a classical case of this kind.

5. All reactions are first-stage reactions, i.e. are held back by the stage of forming the intermediate complex. This is confirmed by the fact that in Figures 4 and 5 the intersecting lines are to the left of the maxima of the volcanolike curves.

6. The mean, and not individual, values of the bond energies are taken. This is justified by the fact that compensation of the effect of neighboring atoms on Q_{AB} etc. and on Q_{AK} etc. occurs to an appreciable extent [34]. When there are great variations there is no such approximate compensation, and this has been noted above, for example, for the effect of the aromatic nucleus.

7. The activation energies used in the calculation are true values, not apparent. This is confirmed by the fact that the process occurs in the kinetic region (see above) and that in the simplest cases the relative adsorption coefficients are not great, and calculation shows that in these cases the percentage conversion can be taken instead of rate constants. For more precise results it is essential to use the full formula.

8. It is assumed that proportionality coefficient in Equation 6 is 3/4. It should be noted that the value of Q_{EK} is not very sensitive to small changes in this coefficient; thus, a calculation in which the coefficient is given the value of unity gives an only slightly different value of Q_{EK}. It should be noted also that Semenov [4], using an independent method, again arrives at a coefficient of 3/4 for a similar case.

The following question now arises. When the energies of the bonds formed with the catalyst have been determined, in what way can they be utilized? It is clear that when many such values are known for substances of various chemical nature and when the laws relating them to the method of preparation are known it will be possible to make use of values of Q_{EK} in the selection of catalysts by the method indicated above, but even now the existing data permit us to solve the problem that is symmetrical with respect to the problems of choice of catalysts.

In the selection of catalysts the reaction is fixed and catalysts are sought for it. In the symmetrical problem we may fix the catalyst and determine what reactions can proceed on it and to what extent.

In this connection the present author and Ponomarev [61] have examined the reactions of furan derivatives over a catalyst of a given chemical nature – nickel – for which the value of Q_{EK} is known. In this case also, the method of volcanolike curves based on the multiplet theory is applicable. It must be particularly emphasized that in the exposition that follows none of the above-mentioned simplifying assumptions are made. The coordinates of the apexes of the volcanolike curves for the reactions occurring are given in Table 3. Values of E′ are also given in the table. The calculation was made with the aid of Equation 5 and was based on values of Q from a previous paper [47] and on a value for the energy of the stabilization of the furan ring of σ = 16 kcal [62].

Table 3

Theoretical Sequence of Reactions over a Nickel Catalyst

No.	Reaction	Doublet scheme	u(kcal)	s(kcal)	E′ (kcal)
1	Hydrogenation of the olefin bond	$\begin{array}{cc}C & H\\ \Vert & \vert\\ C & H\end{array}$	30	318	6
2	Hydrogenation of the carbonyl bond	$\begin{array}{cc}C & H\\ \Vert & \vert\\ O & H\end{array}$	15	379	5
3	Hydrogenation of the first double bond in the furan ring	$\begin{array}{cc}C & H\\ \Vert & \vert\\ C(f) & H\end{array}$	11.4	334	<5.7; 3
4	Formation of a spiro compound from furfuryl alcohol	$\begin{array}{cc}C & O\\ \Vert & \vert\\ C & H\end{array}$	6	308	<5; 2
5	Hydrogenolysis of the carbon-oxygen bond	$\begin{array}{cc}C & H\\ \vert & \vert\\ O & H\end{array}$	24	370	−1
6	Hydrogenolysis of the carbon-carbon bond	$\begin{array}{cc}C & H\\ \vert & \vert\\ C & H\end{array}$	12	336	−42

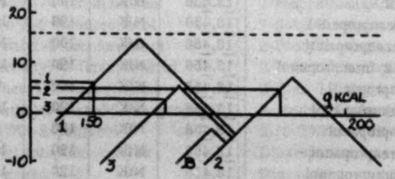


Fig. 5. Volcanolike curves for the hydrogenation of furan and benzene derivatives. (For numbering of the reactions see Table 3. E and q are in kcal).

In Fig. 5 the volcanolike curves are drawn to scale for reactions No. 1, 2, and 3. In addition, the pair of lines B for the hydrogenation of benzene (σ = 36 kcal) are given. Some inferences relating to the furan and benzene rings are based on the obvious fact that no point of the curve lies above the apex, i.e., $E' \leqslant u/2$. Hence, from Equation 5 and the value of u, which involves σ, it is possible to find the upper limit of E′ for the hydrogenation of the C=C bond in the furan and benzene rings. Over Ni this limit is found to be lower for a bond in the ring than E for the same reaction in a chain, and it is lower in the benzene ring than in the furan ring. For several reasons, the zero level is displaced upward by about 16 kcal [46] (broken line in Fig. 5). Hence, all the values of E′ in Table 3 are actually negative. In the cyclization of a furan compound to form a spiran, one (external) double bond in the furan ring is first hydrogenated [63]; in reaction No. 4 (for the numbering of the reactions see Table 3) occurring at the surface, the valency angle is deformed, so that the value of E′ is lowered somewhat. Corrected values of E′ for reactions No. 3 and 4 are also given in Table 3.

Thus, the multiplet theory leads us to the following rule: in the hydrogenation of furan derivatives the reactions occur in a definite sequence according to the difficulty with which they proceed, i.e., in order of diminishing E′ (Table 3). For example, in accordance with the rule, in the hydrogenation of 1-(2-furyl)-1-penten-3-one

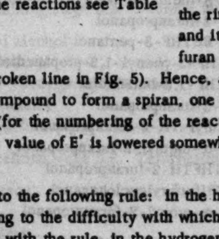


TABLE 4

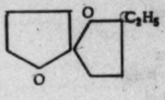
Sequence of Reactions in the Hydrogenation of Furan Compounds over Nickel (Comparison of experimental and theoretical data). Abbreviations: F = 2-furyl; TH = tetrahydro; dioxaspiran = 1,6-dioxaspiro[4.4]nonane; NiR = = Raney nickel; NiK = Ni on kieselguhr

Original substance	Substance formed	A	Catalyst	Temp. (°C)	Pressure (atm)
1	2	3	4	5	6
	Transformations attaining stage 1,2. Average temperature 30°				
2-Furanacrolein	2-Furanpropionaldehyde	1,236	NiR	23	100
4-F-3-buten-2-one	4-F-2-butanone	1,236	NiR	20	50
1-F-8-methyl-1-octen-3-one	1-F-3-octanone	1,236	NiR	20	1
1,3-DiF-2-propen-1-one	1,3-DiF-1-propanone	1,236	NiR	50	100
1,5-DiF-1,4-pentadien-3-one	1,5-DiF-3-pentanone	1,236	NiR	20	1
	Transformations attaining stage 1,3. Average temperature 40°				
Vinylfuran	Ethylfuran	1,36	NiK	65	250
"	"	1,36	NiR	15	75
	Transformations attaining stage 2,3. Average temperature 85°				
2-Furaldehyde	Furfuryl alcohol	$2,3\underline{5}6$	Ni	160	65
2-Furanacrolein	2-Furanpropanol	$12,3\underline{5}6$	NiR	80	–
6-F-3,5-hexadien-2-one	α-Methyl-2-furanpentanol	$12,3\underline{5}6$	NiR	20	1
	Transformations attaining stage 3,2*				
1-F-5-methyl-1-hexen-3-one	5-Methyl-1-THF-3-hexanone*	$13,2\underline{5}6$	Ni	–	–
Furfurylidenecamphor	THfurfurylcamphor*	$13,2\underline{5}6$	Ni	–	–
	Transformations attaining stage 3,4. Average temperature 130°				
2-Furanpropanol	TH-2-furanpropanol	$\underline{1}3,\underline{4}56$	NiK	100	150
5-Methyl-2-furanpropanol	TH-5-methyl-2-furanpropanol	$\underline{1}3,\underline{4}56$	NiK	120	150
α-Methyl-2-furanpropanol	TH-α-methyl-2-furanpropanol	$\underline{1}3,\underline{4}56$	NiK	100	150
α,5-Dimethyl-2-furanpropanol	TH-α,5-dimethyl-2-furanpropanol	$\underline{1}3,\underline{4}56$	NiK	120	128
α-Ethyl-2-furanpropanol	α-EthylTH-2-furanpropanol	$\underline{1}3,\underline{4}56$	NiK	120	96
α-Propyl-2-furanpropanol	TH-α-propyl-2-furanpropanol	$\underline{1}3,\underline{4}56$	NiK	120	120
α-Butyl-2-furanpropanol	α-ButylTH-2-furanpropanol	$\underline{1}3,\underline{4}56$	NiK	120	99
α-Pentyl-2-furanpropanol	TH-α-pentyl-2-furanpropanol	$\underline{1}3,\underline{4}56$	NiK	120	150
α-Isohexyl-2-furanpropanol	α-IsohexylTH-2-furanpropanol	$\underline{1}3,\underline{4}56$	NiK	120	103
α-Phenyl-2-furanpropanol	TH-α-phenyl-2-furanpropanol	$\underline{1}3,\underline{4}56$	NiK	125	142
α-Phenethyl-2-furanpropanol	TH-α-phenethyl-2-furanpropanol	$\underline{1}3,\underline{45}6$	NiK	120	142
β-Methyl-α-phenyl-2-furanpropanol	TH-β-methyl-α-phenyl-2-furanpropanol	$\underline{1}3,\underline{45}6$	NiK	140	110
2-Furanpropionaldehyde	TH-2-furanpropanol	$\underline{1}23,\underline{45}6$	NiK	160	150
1,5-DiF-3-pentanol	1,5-BisTHF-3-pentanol	$13,\underline{45}6$	NiR	120	100
1,F-3-phenyl-1,3-propanedione	1-THF-3-phenyl-1,3-propanediol	$\underline{1}23,\underline{45}6$	NiR	125	170
1-F-1,3-butanedione	1-THF-1,3-butanediol				
2-Furanacrolein	TH-2-furanpropanol	$\underline{1}23,\underline{45}6$	NiR	160	150
α-Ethyl-2-furanacrolein	β-Ethyl-TH-2-furanpropanol	$\underline{1}23,\underline{45}6$	NiR	175	150
4-F-3-buten-2-one	TH-α-methyl-2-furanpropanol	$123,\underline{45}6$	Ni	125	100
1,3-DiF-2-propen-1-one	α-THFTH-2-furanpropanol	$123,\underline{45}6$	NiR	130	115
Difurfurylidenecyclohexanone	BisTHfurfurylcyclohexanol	$123,\underline{45}6$	NiR	175	150
1-F-1-hexen-3-one	TH-α-propyl-2-furanpropanol	$123,\underline{4}56$	NiR	200	70
	Transformations attaining stage 3,5. Average temperature 130°				
Furan	THfuran Butyl alcohol	$\underline{1}3,\underline{5}6$	NiR	170	–
2-Methylfuran	TH-2-methylfuran	$\underline{1}3,\underline{5}56$	Ni	200	–

TABLE 4 (continued)

1	2	3	4	5	6
2-Ethylfuran	2-EthylTHfuran	$\underline{1}3,\underline{5}6$	NiR	<110	70
2-Propylfuran	TH-2-propylfuran	$\underline{1}3,\underline{5}6$	NiR	<110	70
2-Pentylfuran	TH-2-pentylfuran	$\underline{1}3,\underline{5}6$	NiR	110	70
2-(1-Butenyl)furan	2-ButylTHfuran	$\underline{1}3,\underline{5}6$	NiR	100	50
2-Benzylfuran	2-BenzylTHfuran	$\underline{1}3,\underline{5}6$	Ni	100	50
2,5-Dimethylfuran	TH-2,5-dimethylfuran	$\underline{1}3,\underline{5}6$	NiR	200	70
Furfuryl alcohol	THfurfuryl alcohol	$\underline{1}3,56$	NiR	80	80
α-Methylfurfuryl alcohol	TH-α-methylfurfuryl alcohol	$\underline{1}3,56$	NiR	75	10
α-Ethylfurfuryl alcohol	α-EthylTHfurfuryl alcohol	$\underline{1}3,56$	NiR	65	80
α-Propylfurfuryl alcohol	TH-α-propylfurfuryl alcohol	$\underline{1}3,56$	NiR	65	80
α-Phenylfurfuryl alcohol	TH-α-phenylfurfuryl alcohol	$\underline{1}3,56$	NiK	65	80
α-Methyl-2-furanpentanol	TH-α-methyl-2-furanpentanol	$\underline{1}3,56$	NiK	120	90
2-Furaldehyde diethyl acetal	TH-2-furaldehyde diethyl acetal	$\underline{1}3,56$	NiR	175	—
2-Furaldehyde ethylene acetal	TH-2-furaldehyde ethylene acetal	$\underline{1}3,56$	NiK	125	150
Furoin	1,2-BisTHF-1,2-ethanediol	$\underline{1}23,56$	NiR	150	150
5-(Hydroxymethyl)-2-furaldehyde	TH-2,5-furandimethanol	$\underline{1}23,56$	NiK	160	70
2-Furaldehyde	THfurfuryl alcohol	$\underline{1}23,56$	NiK	125	40
5-F-2,4-pentadienal	TH-2-furanpentanol	$123,\underline{5}6$	NiR	175	150
6-F-3,5-hexadien-2-one	TH-α-methyl-2-furanpentanol	$123,\underline{5}6$	NiR	175	150
7-F-4,6-heptadien-3-one	α-EthylTH-2-furanpentanol	$123,\underline{5}6$	NiR	140	100
1 9-DiF-1,3,6,8-nonatetraen-5-one	1,9-BisTHF-5-nonanol	$123,\underline{5}6$	NiR	175	180
Transformations attaining stage 4,5. Average temperature 130°					
2-Furanpropanol	Dioxaspiran	$\underline{1}3\underline{4},56$	NiK	100	150
α-Methyl-2-furanpropanol	2-Methyldioxaspiran	$\underline{1}3\underline{4},56$	NiK	100	150
5-Methyl-2-furanpropanol	2-Methyldioxaspiran	$\underline{1}3\underline{4},56$	NiK	120	150
α,5-Dimethyl-2-furanpropanol	2,7-Dimethyldioxaspiran	$\underline{1}3\underline{4},56$	NiK	120	140
α-Ethyl-2-furanpropanol	2-Ethyldioxaspiran	$\underline{1}3\underline{4},56$	NiK	120	96
α-Propyl-2-furanpropanol	2-Propyldioxaspiran	$\underline{1}3\underline{4},56$	NiK	120	128
α-Butyl-2-furanpropanol	2-Butyldioxaspiran	$\underline{1}3\underline{4},56$	NiK	120	99
α-Pentyl-2-furanpropanol	2-Pentyldioxaspiran	$\underline{1}3\underline{4},56$	NiK	120	150
α-Isohexyl-2-furanpropanol	2-Isohexyldioxaspiran	$\underline{1}3\underline{4},56$	NiK	120	103
α-Phenyl-2-furanpropanol	2-Phenyldioxaspiran	$\underline{1}3\underline{4},56$	NiK	125	142
β-Methyl-α-phenyl-2-furanpropanol	3-Methyl-2-phenyldioxaspiran	$\underline{1}3\underline{4},56$	NiK	140	110
1,5-DiF-3-pentanol	2-(2-THFethyl)dioxaspiran	$\underline{1}3\underline{4},56$	NiR	120	105
2-Furanpropionaldehyde	Dioxaspiran	$\underline{1}23\underline{4},56$	NiK	160	150
2-Furanacrolein	Dioxaspiran	$123\underline{4},56$	NiR	175	150
α-Ethyl-2-furanacrolein	3-Ethyldioxaspiran	$123\underline{4},56$	NiR	175	150
4-F-3-buten-2-one	2-Methyldioxaspiran	$123\underline{4},56$	NiR	175	150
Transformations attaining stage 5,5. Average temperature 190°					
THfuran	Butyl alcohol	5,56	NiR	90	155
2-Methylfuran	2-Pentanol	$\underline{1}3\underline{5},\underline{5}6$	NiR	200	—
3-F-acrylophenone	2-(3-Phenylpropyl)THfuran	$\underline{1}23\underline{5},\underline{5}6$	NiR	140	135
TH-2-methylfuran	2-Pentanol	5,56	Ni	230	140
Dioxaspiran	TH-2-furanpropanol	5,56	NiK	200	150
Transformations attaining stage 5,6. Temperature > 310°					
2-Furanacrolein	Heptane	12345,6	NiO+ +MoS_2	310	100
2-Furanacrolein	Heptane	12345,6	Ni	> 300	100
α-Methylfurfuryl alcohol	Heptane	12345,6	NiO+ +MoS_2	340	100
Furan	Butane	135,6	Ni	> 300	—
THfuran	Butane	35,6	Ni	> 300	—

over nickel the following should be formed successively: 1) 1-(2-furyl)-3-pentanone; 2) α-ethyl-2-furanpropanol; 3) α-ethyltetrahydro-2-furanpropanol; 4) 2-ethyl-1,6-dioxaspiro[4.4]nonane



5) nonane; and 6) methane.

Verification of this rule on the basis of experimental material is carried out in Table 4. The numbers in the column headed A, for example 123,456 indicate that in the given change reactions No. 1, 2, and 3 (Table 3) have already occurred, but the reactions No. 4, 5, and 6 have not yet occurred, the change having attained the stage 3,4. Here, each of the reactions No. 1, 2, and 3 proceeds more readily than each of the reactions No. 4, 5, and 6. Underlined digits in Table 4 indicate secondary reactions that are possible owing to the completion of primary reactions: 1 → 6, 2 → 5; 3 → 1,4 and 6; 4 → 5 and 6. In A numbers on one side of the comma are not repeated. Reactions that depend on reactions that have not yet occurred are not shown in A. When the digits in column A of Table 4 are in ascending order (or do not diminish), it means that the theoretical rule that we have found is correct. Table 4 gives the known examples [61] of the changes undergone by furan compounds when hydrogenated over Ni (apart from those of a few containing the groups —(CO)—O— and —N—).

Table 4 shows that theory is in excellent agreement with experiment for more than 80 transformations. Exceptions are rare; they are indicated in the table by asterisks.

It will be seen from Table 4 that in all cases in which a molecule contains both a furan and a benzene ring, the former is more readily hydrogenated, in accord with the requirements of theory.

It can also be seen from Table 4 that, in accord with theoretical predictions, the temperature required for the reaction is generally higher, the higher the number of the reaction in Table 3. This is all the more remarkable in that the hydrogenation reactions of furan compounds have been carried out independently by various workers, who had only preparative aims in view. In accordance with theory, different sequences are found over other catalysts [66, 67].

The discovery of the laws regulating the hydrogenation of furan derivatives is of great practical importance, since these processes are associated with a new important trend in the industrial utilization of agricultural wastes.

In conclusion I should like to appeal to those present to join forces in working for the solution of the particularly important problem of the scientific selection of catalysts. The object of this paper was to show what foundations exist for this work. It must be remembered that in the discussions experiment must be the judge and that the general goal of our endeavors is the welfare of our Fatherland.

Received April 23, 1955

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

LITERATURE CITED

[1] G. K. Boreskov, Catalysis in the Manufacture of Sulfuric Acid, State Chem. Press, Moscow, 1954.

[2] P. H. Emmett, Catalysis, 1. Fundamental Principles, N. Y., 1954.

[3] Advances in Catalysis, 6, N. Y., 1954.

[4] N. N. Semenov, Some Problems of Chemical Kinetics and Reactivity, Acad. Sci. USSR Press, Moscow, 1954.

[5] J. chim. phys. biol., No. 9-12 (1954).

[6] Conference on Catalytic Hydrogenation and Oxidation. Summary of Papers. Alma Ata, 1954.

[7] Problems of Soviet Science. Scientific Basis of the Selection of Catalysts. Moscow, 1954.

[8] B. A. Kazansky, A. L. Liberman, V. T. Aleksanyan and Kh. E. Sterin, Proc. Acad. Sci. USSR, 95, 281 (1954).

[9] N. I. Shuikin and V. A. Tulupov, Proc. Acad. Sci. USSR, 100, 731 (1955).

[10] A. A. Ponomarev, Doctorate thesis, Moscow State Univ., 1954.

[11] L. Kh. Freidlin and K. G. Rudneva, Proc. Acad. Sci. USSR, 91, 569, 1349 (1953); Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, 3, 491. [T.p. 417].*

[12] D. V. Sokolsky, Bull. Acad. Sci. Kazakh. SSR No. 8, 65 (1954).

[13] M. B. Turova-Polyak, N. V. Danilova and E G. Treshchova, J. Gen. Chem., 24, 1558 (1954).

[14] R. Ya. Levina, Bull. Moscow Univ., 12, 71 (1954).

[15] Yu. K. Yuryev, Proc. Acad. Sci. USSR, 94, 265 (1954).

[16] V. A. Maslennikova and S. A. Sultanov, Proc. Acad. Sci. Uzbek. SSR, 3, 35 (1954).

[17] N. S. Kozlov and N. I. Panova, J. Gen. Chem., 24, 317 (1954). [T.p. 323]*

[18] K. V. Topchieva, Bull. Moscow Univ., No. 8, 107 (1954); K. V. Topchieva, A. P. Ballod, I. V. Patsevich and N. N. Rtishcheva, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 3, 478. [T.p. 405].*

[19] Oil and Gas J., 27, III; 27.7, 19.8 (1953); Petroleum, No. 5 (1953).

[20] N. D. Zelinsky, Selected Works, 2. Catalysis, Acad. Sci. USSR Press, Moscow, 1941.

[21] M. Bodenstein, Ann. 440, 177 (1924).

[22] P. Sebatier, Catalysis in Organic Chemistry, Leningrad, 1932.

[23] E. K. Rideal, Chem. Ind., 335 (1943).

[24] G. K. Boreskov, Problems of Kinetics and Catalysis, 6, 404 (1949).

[25] A. A. Balandin, Jubilee Collection devoted to the Thirtieth Anniversary of the Great October Socialist Revolution, Vol. 1, Acad. Sci. USSR Press, 1947, p. 637.

[26] H. S. Taylor, J. Phys. Chem., 30, 145 (1926); Disc. Faraday Soc., 8, 9 (1950).

[27] M. I. Temkin, J. Phys. Chem., 11, 169 (1938).

[28] S. Z. Roginsky, Adsorption and Catalysis on Nonuniform Surfaces, Acad. Sci. USSR Press, Moscow, 1948.

[29] N. I. Kobozev, Sci. Mem. Moscow State University, 86, 131 (1946).

[30] S. Z. Roginsky, J. Appl. Chem., 17, 1, 19 (1944).

[31] S. Z. Roginsky and F. F. Volkenshtein, Trans. All-Union Conference on Catalysis, Kiev, 1950, p. 9.

[32] M. I. Temkin, J. Phys. Chem., 11, 169 (1938).

[33] S. Glasstone, K. Laidler and H. Eyring, Theory of Absolute Reaction Rates, Foreign Lit. Press, Moscow, 1948.

[34] A. A. Balandin, Proc. Acad. Sci USSR, 97, 667 (1954).

[35] B. M. W. Trapnell, Adv. in Catalysis, 3, 1 (1951).

[36] J. H. Long, I. C. W. Frazer, F. Ott, J. Am. Chem. Soc., 56, 1101 (1934).

[37] P. H. Emmett, N. Skau, J. Am. Chem. Soc., 65, 1029 (1943).

[38] G. Rienäcker, S. Unger, Z. anorg. Chem., 274, 47 (1953).

[39] A. M. Rubinshtein, N. I. Shuikin and Kh. M. Minachev, Proc. Acad. Sci. USSR, 67, 287 (1948).

[40] O. Beeck, Rev. Mod. Phys., 17, 79 (1945).

[41] W. M. H. Sachtler, G. Dorgelo, W. van der Knaap, J. chim. phys. biol., 51, 491 (1954).

---

* T.p. = Consultants Bureau Translation pagination.

[42] G. C. A. Schuit, N. H. de Boer, J. chim. phys. biol., 51, 482 (1954).

[43] A. A. Balandin and G. V. Isagulyants, Proc. Acad. Sci. USSR, 63, 109, 271 (1948); 64, 207 (1949).

[44] C. Kemball, Advances in Catalysis, 2, 233 (1950).

[45] A. A. Balandin, Proc. Acad. Sci. USSR, 97, 449 (1954).

[46] A. A. Balandin, J. Gen. Chem., 16, 793 (1946).

[47] A. A. Balandin, J. Gen. Chem., 42, 337 (1942).

[48] A. A. Balandin, J. Gen. Chem., 62, 703 (1930).

[49] A. A. Balandin and V. V. Patrikeev, J. Gen. Chem., 11, 22 (1941).

[50] A. A. Balandin, J. Phys. Chem., 14, 1160 (1940).

[51] A. A. Balandin, Proc. Acad. Sci. USSR, 93, 55 (1953).

[52] A. A. Balandin, Proc. Acad. Sci. USSR, 93, 273, 475 (1953).

[53] V. N. Kondratyev, Structure of Atoms and Molecules, Acad. Sci. USSR Press, 1946, p. 301.

[54] A. A. Balandin, Prog. Chem., 13, 365 (1944).

[55] S. Berkman, J. Morrell, and G. Egloff, Catalysis in Inorganic and Organic Chemistry, 2, State Fuel Tech. Press, Moscow, 1949, p. 344.

[56] A. A. Balandin and A. A. Tolstopyatova, Proc. Acad. Sci. USSR, 94, 49 (1954).

[57] M. B. Neiman, B. A. Kuznetsov and Yu. M. Shapovalov, Proc. Acad. Sci. USSR, 92, 611 (1953).

[58] A. Kh. Bork, J. Phys. Chem., 14, 1290 (1940).

[59] R. C. Hansford, Advances in Catalysis, 4, 1 (1952).

[60] D. A. Dowden, J. Chem. Soc., 1950, 242.

[61] A. A. Balandin and A. A. Ponomarev, Proc. Acad. Sci. USSR, 100, 917 (1955).

[62] I. B. Conant, G. B. Kistiakowsky, Chem. Rev., 20, 181 (1937).

[63] A. A. Ponomarev, V. A. Afanasyev and N. I. Kurochkin, J. Gen. Chem., 23, 1426 (1953). [T.p. 1493].*

[64] A. A. Ponomarev and V. V. Zelenkova, Prog. Chem., 20, 589 (1951).

[65] H. A. Smith, I. F. Fusek, J. Am. Chem. Soc., 71, 451 (1949).

[66] Yu. K. Yuryev, V. A. Tronova, M. Ya. Kuznetsova, and E. G. Novosadova, J. Gen. Chem., 17, 131 (1947).

---

* T.p. = Consultants Bureau Translation pagination.

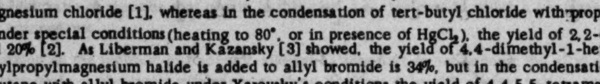
SYNTHESIS OF BRANCHED ALIPHATIC HYDROCARBONS VIA 2-ALKENYL HALIDES

A. D. Petrov

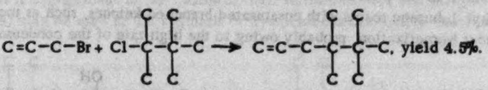
(Paper read at a general meeting of the Division of Chemical Sciences
of the Academy of Sciences of the USSR, March 21, 1955)

2-Alkenyl halides have received extensive application during the last 10-15 years for the synthesis of branched alcohols and hydrocarbons, mainly in connection with the intensive exploitation of organomagnesium synthesis with the object of preparing model individual hydrocarbons present in fuels and oils.

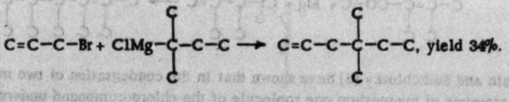
It has been established that 2,2-dimethylpentane is best prepared via 4,4-dimethyl-1-pentene, which can be synthesized in 85% yield, calculated on the amount of allyl bromide taken, by addition to the latter of an ethereal solution of tert-butylmagnesium chloride [1], whereas in the condensation of tert-butyl chloride with propylmagnesium bromide, even under special conditions (heating to 80°, or in presence of $HgCl_2$), the yield of 2,2-dimethylpentane does not exceed 20% [2]. As Liberman and Kazansky [3] showed, the yield of 4,4-dimethyl-1-hexene obtained when 1,1-dimethylpropylmagnesium halide is added to allyl bromide is 34%, but in the condensation of 2-chloro-2,3,3-trimethylbutane with allyl bromide under Yarovsky's conditions the yield of 4,4,5,5-tetramethyl-1-hexene does not exceed 4.5% [4]:



$$\mathrm{C{=}C{-}C{-}Br + Cl\cdot Mg{-}\overset{C}{\underset{C}{C}}{-}C \longrightarrow C{=}C{-}C{-}\overset{C}{\underset{C}{C}}{-}C}, \text{ yield } 85\%. \qquad (1)$$

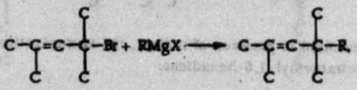


$$\mathrm{C{=}C{-}C{-}Br + Cl{-}\overset{C}{\underset{C}{C}}{-}\overset{C}{\underset{C}{C}}{-}C \longrightarrow C{=}C{-}C{-}\overset{C}{\underset{C}{C}}{-}\overset{C}{\underset{C}{C}}{-}C}, \text{ yield } 4.5\%. \qquad (2)$$



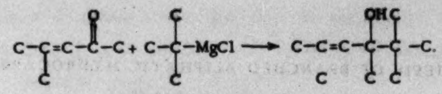
$$\mathrm{C{=}C{-}C{-}Br + ClMg{-}\overset{C}{\underset{C}{C}}{-}C{-}C \longrightarrow C{=}C{-}C{-}\overset{C}{\underset{C}{C}}{-}C{-}C}, \text{ yield } 34\%. \qquad (3)$$

The high reactivity of 2-alkenyl halides found wide application in the work of Levina and coworkers [5], who condensed 4-bromo-2,4-dimethyl-2-pentene, which on account of its structure is unable to undergo the allyl rearrangement, with various alkylmagnesium halides. The reaction gave yields of 25-30%:



$$\mathrm{C{-}\underset{C}{C}{=}C{-}\overset{C}{\underset{C}{C}}{-}Br + RMgX \longrightarrow C{-}\underset{C}{C}{=}C{-}\overset{C}{\underset{C}{C}}{-}R} \qquad (4)$$

Petrov, Koptev and Kaplan [6] showed that steric difficulties in the condensation of a branched ketone with branched alkyl halides could be overcome by introducing a double bond into the ketone, instead of into the alkyl halide, but again in the β-position with respect to the functional group, the oxygen of the carbonyl. Thus, tert-butylmagnesium chloride, which does not give a tertiary alcohol with 4-methyl-2-pentanone, but only reduces it, reacts with mesityl oxide at 0° with formation of a tertiary alcohol and the diolefin resulting from its dehydration:



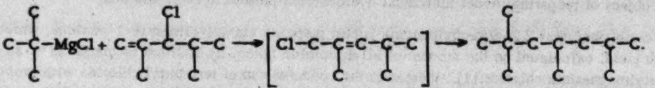
$$\mathrm{C-\underset{C}{C}=C-\overset{O}{\overset{\|}{C}}-C+C-\overset{C}{\underset{C}{C}}-MgCl \longrightarrow C-\underset{C}{C}=C-\overset{OH}{\underset{C}{C}}-\overset{C}{\underset{C}{C}}-C.}$$

(5)

The possibility of increasing the yield by introduction of a double bond in either reaction component greatly widens the prospect for the synthesis of branched compounds.

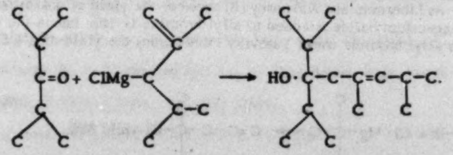
Since there are comparatively few alkenyl halides of the allyl type that are unable to undergo the allyl rearrangement on account of their structure, we frequently meet the problem of suppressing such isomerization either by the selection of a second component of suitable structure or by selection of the condensation conditions.

Petrov and Ponomarenko [7] showed that in the course of the organomagnesium synthesis 3-chloro-2.4-dimethyl-1-pentene isomerizes completely into the corresponding primary chloride in reactions both with tertiary and with primary alkylmagnesium halides and also in the reaction of condensation with 2,4-dimethyl-3-pentanone in presence of magnesium:



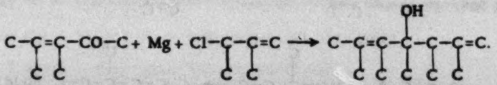
$$\mathrm{C-\overset{C}{\underset{C}{C}}-MgCl+C=\underset{C}{C}-\overset{Cl}{C}-\underset{C}{C}-C \longrightarrow \left[Cl-C-\underset{C}{C}=C-\underset{C}{C}-C\right] \longrightarrow C-\overset{C}{\underset{C}{C}}-C-\underset{C}{C}-C-\underset{C}{C}-C.}$$

(6)



(7)

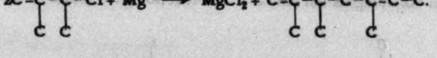
However, as has been shown in the present series of investigations by Petrov and Melekhin, the analogous allyl halide 3-chloro-2-methyl-1-butene reacts with unsaturated branched ketones, such as mesityl oxide and 3-methyl-3-buten-2-one, without isomerization, probably owing to the high rate of the condensation reaction:



$$\mathrm{C-\underset{C}{C}=\underset{C}{C}-CO-C+Mg+Cl-\underset{C}{C}-\underset{C}{C}=C \longrightarrow C-\underset{C}{C}=\underset{C}{C}-\overset{OH}{\underset{C}{C}}-\underset{C}{C}-\underset{C}{C}=C.}$$

(8)

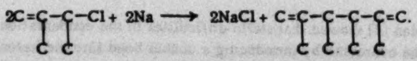
Petrov, Melekhin and Sushchinsky [8] have shown that in the condensation of two molecules of 3-chloro-2-methyl-1-butene in presence of magnesium one molecule of the chlorocompound undergoes allyl rearrangement and 2.3.5-trimethyl-1.5-heptadiene is formed:



$$\mathrm{2C=\underset{C}{C}-\underset{C}{C}-Cl+Mg \longrightarrow MgCl_2+C=\underset{C}{C}-\underset{C}{C}-C-\underset{C}{C}=C-C.}$$

(9)

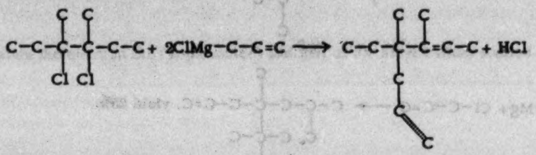
When the same alkenyl halide is condensed in presence of sodium, the isomerization becomes a subordinate reaction and the main product is 2,3,4,5-tetramethyl-1,5-hexadiene:



$$\mathrm{2C=\underset{C}{C}-\underset{C}{C}-Cl+2Na \longrightarrow 2NaCl+C=\underset{C}{C}-\underset{C}{C}-\underset{C}{C}-\underset{C}{C}=C.}$$

(10)

In the condensation of 3-chloro-2-methyl-1-butene in presence of potassium, which is even more alkaline in character than sodium and brings about a more rapid reaction even at lower temperatures, isomerization occurs to an extremely small extent. Hence, the occurrence of the allyl rearrangement can be avoided not only by selecting carbonyl and halogen compounds of suitable structure, but also by selecting suitable conditions of condensation, and this possibility promises to extend greatly the scope of this method of synthesizing branched hydrocarbons. We will give one further example of the effect of the condensation conditions on the character of the products. It was shown recently by Petrov and Shebanova [9] that in the treatment of 3,4-dichloro-3,4-dimethylhexane with allylmagnesium chloride at room temperature condensation occurred with only one molecule of allyl halide with simultaneous elimination of a molecule of HCl:

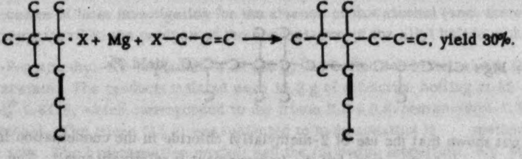


(11)

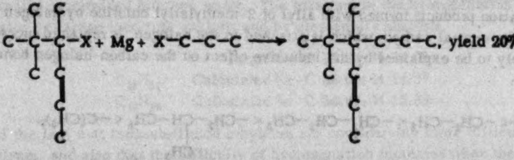
By carrying out the condensation at −10°, we have succeeded in the present investigation in obtaining not only this C_{11} hydrocarbon (in about 15% yield), but also the desired C_{14} diene, which was hydrogenated with formation of 4,5-diethyl-4,5-dimethyloctane.

It was pointed out above that in condensations with ketones having α,β-double bonds (i.e., characterized by π,π-conjugation) even allyl halides that can undergo the allyl rearrangement do not, in fact, isomerize, evidently owing to the particularly high rates of reaction that obtain in this case, i.e., the case in which a conjugated system is found in both reaction components.

Recently, while working on the problem of finding 2-alkenyl halides that do not undergo the allyl rearrangement (on account of various steric or electronic effects) in condensations not only with alkenyl halides but also with alkyl halides, Petrov and Lavrishcheva [10] made the following observation. It was found that the tertiary alcohol synthesized from pinacolone and BrMgC−C=C forms an active halogen derivative having a double bond in the β-position, and that this reacts with RMgX (R may be allyl or propyl) without undergoing the allyl rearrangement. This peculiarity of the halogen compound is not shared by such compounds as 4-bromo (or chloro)-4-methyl-1-pentene (in the formation of which the double bond is not displaced from the allyl to the propenyl position, so that these halogen compounds are inactive), nor by other tertiary halogen compounds containing allyl radicals and undergoing the allyl rearrangement in the course of their formation, and this halogen compound (4-chloro-4,5,5-trimethyl-2-hexene) may be used in the synthesis of hydrocarbons containing two adjacent quaternary carbons:

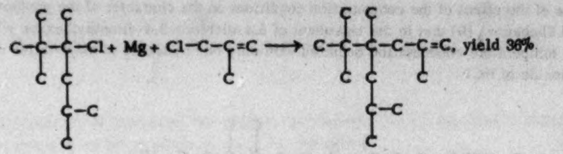


(12)

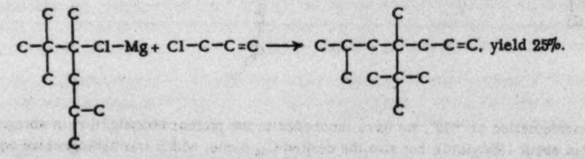


(13)

The high yields attained (in comparison with those obtained in the condensation of an allyl halide with 2-chloro-2,3,3-trimethylbutane (Equation 2) were at first attributed by us solely to the occurrence of σ,π-conjugation in both components in the first case, but in one component only in the second. Continuing this investigation, Petrov and Sushchinsky replaced allyl by 2-methylallyl in the tertiary halide, but this made it necessary to hydrogenate the unsaturated tertiary alcohol before its conversion into the halogen compound. The reactions of Equations 14 and 15 were carried out, and it was found that saturated but asymmetrical tertiary chloro compounds analogous to 2-chloro-2,3,3-trimethylbutane give condensation products in yields that differ little from those obtained from 2-alkenyl halides of the same structural type.

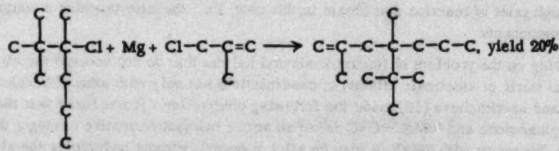


(14)

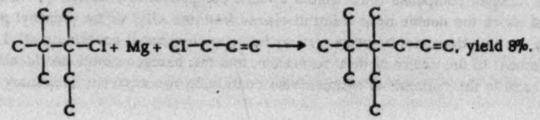


(15)

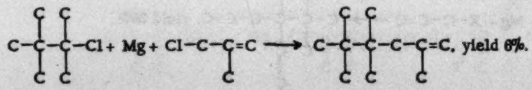
Somewhat lower yields were obtained when the isobutyl radical in the tertiary halide was replaced by propyl and, particularly, by ethyl (Equations 16 and 17):



(16)



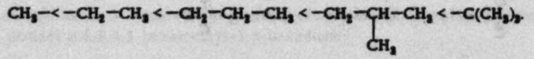
(17)



(18)

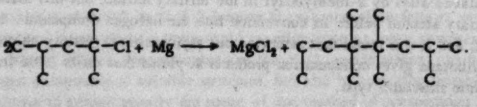
$$C-\underset{C}{\overset{C}{C}}-\underset{C}{\overset{C}{C}}-Cl + Mg + Cl-C-\underset{C}{C}=C \longrightarrow C-\underset{C}{\overset{C}{C}}-\underset{C}{\overset{C}{C}}-C-\underset{C}{C}=C, \text{ yield } 6\%. \tag{18}$$

At the same time, it was shown that the use of 2-methylallyl chloride in the condensation instead of allyl chloride results in some improvement in the yield, but the improvement is relatively small. The increase of the yields in a series of condensation products formed with allyl or 2-methylallyl chloride by halogen compounds in which a methyl standing at the central carbon, which is attached to the halogen, is replaced successively by ethyl, propyl and isobutyl is probably to be explained by the inductive effect on the carbon-halogen bond, which is known [11] to increase in the series:



$$CH_3- < -CH_2-CH_3 < -CH_2-CH_2-CH_3 < -CH_2-\underset{CH_3}{CH}-CH_3 < -C(CH_3)_3.$$

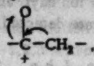
It is interesting also to note that the reaction of Equation 19 went with a yield of 6%, whereas hexamethylethane is obtained in only 3% yield under these conditions, and octamethylhexane is not formed at all.



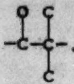
(19)

$$2C-\underset{C}{C}-C-\underset{C}{\overset{C}{C}}-Cl + Mg \longrightarrow MgCl_2 + \underset{C}{C}-C-\underset{C}{\overset{C}{C}}-\underset{C}{\overset{C}{C}}-C-\underset{C}{C}-C. \tag{19}$$

It is possible that the high yields obtained in the reactions of Equations 14, 15, 16 and 19 are to be attributed not only to the inductive effect, but also to σ,σ-conjugation, but in order to prove the existence of this effect further investigations are necessary. We may note, however, the parallelism existing between the reactivity of ketones (high when the hydrogens on the α-C are unsubstituted

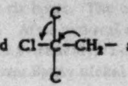


, and low when they are substituted

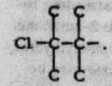


$-\overset{\overset{O}{|}}{C}-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-$

, i.e., when the electron shift is prevented) and that of the alkyl halides studied



and



$Cl-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-$.

EXPERIMENTAL

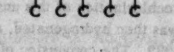
2,3,4,5,6-Pentamethylheptane. From 108 g of acetyl chloride and 98 g of 2-methyl-2-butene, 72 g of 3,4-dimethyl-3-penten-2-one (b.p. 146-147°, n_D^{20} 1.4472; d_4^{20} 0.8678) was prepared by Kondakov's method [12]. A mixture of the product (72 g) and 94 g of 3-chloro-2-methyl-1-butene as a solution in 300 ml of ether was added with stirring to 50 g of magnesium in 300 ml of ether. Stirring was continued for 70 hours without the application of heat, and decomposition was then effected with ammonium chloride solution and ice. Ether was distilled off at atmospheric pressure, and at reduced pressure the C_{10} diene fraction came over up to 65° (7 mm) and was followed by 56 g (48%) of a fraction boiling at 76-77° (7 mm) and having n_D^{20} 1.4710 and d_4^{20} 0.8833; this was the tertiary alcohol, 2,3,4,5,6-pentamethyl-1,5-pentadien-4-ol (or, if the allyl halide underwent isomerization, 2,3,4,6-tetramethyl-2,6-octadien-4-ol).

The alcohol (15 g) was oxidized with a 2% potassium permanganate solution. Among the neutral oxidation products, acetone (its 2,4-dinitrophenylhydrazone gave no depression with that of acetone) and 2,3-butanedione (2,4-dinitrophenylhydrazone, m.p. 314-315°) were identified. In the evaporated solution of salts only formic acid (no acetic) was detected, and it was determined quantitatively by the calomel method (1.1633 g). The isomeric 2,3,4,6-tetramethyl-2,6-octadien-4-ol should have yielded acetone, 2,3-butanedione, and acetic acid, so that our only evidence for the absence of this alcohol and, therefore, of the non-occurrence of the allyl rearrangement rests on the results of the investigation of the acid fraction. It is fortunate that we were able to obtain supplementary evidence in the course of later investigation for the absence of this alcohol (and, therefore, for the non-occurrence of the allyl rearrangement) in the products of the condensation of the allyl halide with the unsaturated ketone.

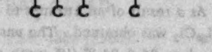
2,3,4,5,6-Pentamethyl-1,5-heptadien-4-ol (40 g) was boiled for 30 hours with 69 g of acetic anhydride and 27 g of sodium acetate. The products isolated were 15.3 g of a fraction boiling at 55-56° (7 mm) and having n_D^{20} 1.4650 and d_4^{20} 0.8118, which corresponded to the triene 2,3,4,5,6-pentamethyl-1,3,5-heptatriene, and 10.2 g of unchanged alcohol. The triene (15 g) was subjected to hydrogenation in methanol solution over Raney nickel at 169° and 120 atm. The hydrogenation product had the following properties: b.p. 60-68° (10 mm); n_D^{20} 1.4418; d_4^{20} 0.7862; it readily decolorized bromine water. The presence in the hydrogenation product of one double bond was confirmed also by Raman spectrum analysis and by elementary analysis.

Found %: C 85.25; H 14.69
$C_{12}H_{24}$. Calculated %: C 85.63; H 14.37
$C_{12}H_{26}$. Calculated %: C 84.61; H 15.39

In view of the fact that tetrasubstituted ethylenes are considerably more difficult to hydrogenate than disubstituted ethylenes, and also that the difficulty of hydrogenation increases when the double bond is moved to the center of the molecule, we supposed that the hydrogenation product was 2,3,4,5,6-pentamethyl-3-heptene (I) with some admixture of 2,3,4,6-tetramethyl-2-octene (II) (though only if at least partial allyl rearrangement had occurred)



$C-\underset{\underset{C}{|}}{C}-\underset{\underset{C}{|}}{C}=\underset{\underset{C}{|}}{C}-\underset{\underset{C}{|}}{C}-\underset{\underset{C}{|}}{C}-C.$ (I)



$C-\underset{\underset{C}{|}}{C}=\underset{\underset{C}{|}}{C}-\underset{\underset{C}{|}}{C}-C-\underset{\underset{C}{|}}{C}-C-C.$ (II)

In order to establish the structure of the olefin, it was subjected to permanganate oxidation. In the cold, oxidation proceeded with difficulty: the hydrocarbon was not oxidized even with a 6% solution of potassium permanganate. It was oxidized at the boil for ten days, and 4.7 g of the hydrocarbon gave the following neutral oxidation products (no acid oxidation products were detected):

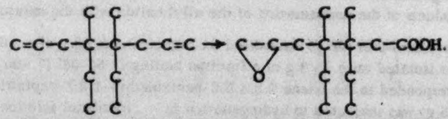
Fraction I, b.p. 77-98°; 0.2 g; n_D^{20} 1.3881
Fraction II, b.p. 120-130°; 0.2 g; n_D^{20} 1.4134
Fraction III, b.p. 62-65° (10 mm); 1.4 g; n_D^{20} 1.4412

Fraction I gave a precipitate with 2,4-dinitrophenylhydrazine: the product melted at 116-117° after four recrystallizations and gave no depression in admixture with the 2,4-dinitrophenylhydrazone of 3-methyl-2-butanone. Fraction II gave a 2,4-dinitrophenylhydrazone of m.p. 101-102°, which corresponds [13] to the dinitrophenylhydrazone of 3,4-dimethyl-2-pentanone. The absence in the oxidation products of acetone and of a C_9 ketone may be taken as proof that there is no olefin (II) present in the olefin investigated. Fraction III was found to be unoxidized olefin. When a more active catalyst than nickel was used, namely palladium on silica gel, over which the olefin was treated at 163° and 124 atm, it was found possible to convert it into the paraffin hydrocarbon 2,3,4,5,6-pentamethylheptane, b.p. 64-66° (11 mm); n_D^{20} 1.4392; d_4^{20} 0.7838; freezing point below −80° (freezes to a glass).

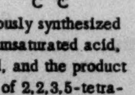
4,5-Diethyl-4,5-dimethyloctane. An ethereal solution of 100 g of 3,4-dichloro-3,4-dimethylhexane and 152 g of allyl chloride was added dropwise to 48 g of magnesium. At the beginning of the addition the small amount of chloro compounds present was heated to the boiling point of ether, but when the reaction began the water bath was replaced by an acetone bath in which a temperature of −20° was maintained throughout the addition operation. After decomposition of the reaction product and removal of ether, two fractions were sepatated by fractional distillation:

Fraction I, b.p. 178-180° (760 mm); yield 38%; n_D^{20} 1.4560; d_4^{20} 0.802.
Fraction II, b.p. 210-215° (760 mm); yield 10%; n_D^{20} 1.4620; d_4^{20} 0.818.

When Fraction II was oxidized with a 1% solution of potassium permanganate, only acid oxidation products were obtained. Among these formic acid was identified, and fractional precipitation with silver nitrate gave the silver salt of an acid containing 31.82% Ag. For the salt of an epoxy acid $C_{13}H_{22}O_3Ag$ the percentage of silver would be 32.2. The epoxy acid was evidently formed according to the scheme:



The fraction of b.p. 210-215° was hydrogenated over Raney nickel at 190° and 200 atm. The hydrogenation product boiled at 216-218°, had a freezing point of below −80°, and had n_D^{20} 1.4440, and d_4^{20} 0.798.

4-tert-Butyl-2,4,6-trimethylheptane. The reactants were magnesium (73 g), pinacolone (100.3 g), and 2-methylallyl chloride (135 g). The reaction was carried out in accordance with Yarovsky's procedure. The product was 142 g of 2,2,3,5-tetramethyl-4-hexen-3-ol, b.p. 46° (4 mm); n_D^{20} 1.4502; d_4^{20} 0.8514. Whitmore [14] has previously prepared an alcohol of this structure, but by another method (reaction of mesityl oxide with tert-butylmagnesium chloride) and in considerably lower yield, and he reported very similar physical properties. The structure of the alcohol, which, on account of the displacement of the double bond, was 2,2,3,5-tetramethyl-4-hexen-3-ol, was proved by oxidation, the identified products being acetone and the crystalline hydroxy acid  $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}\overset{OH}{\underset{C}{C}}{-}COOH}$, m.p. 141°, previously described by Petrov and Lavrishcheva [10]. A mixture test with the previously synthesized acid showed no depression. As a result of an attempt to carry out the hydrochlorination of this unsaturated acid, the dichloro compound $C_{10}H_{20}Cl_2$ was obtained. The unsaturated alcohol was then hydrogenated, and the product had the following properties: b.p. 84.6-84.8° (25 mm); n_D^{20} 1.4368; d_4^{20} 0.8393. The conversion of 2,2,3,5-tetramethyl-3-hexanol into its hydrochloric ester was carried out by the passage of HCl at 0°. The chlorocompound boiled at 72.6–73.5° (28 mm) and had n_D^{20} 1.4455 and d_4^{20} 1.8778. This chloro compound was condensed with 2-methylallyl chloride by Yarovsky's method. The condensation product had the following properties: b.p. 92.5° (12 mm); n_D^{20} 1.4584; d_4^{20} 0.8163; its hydrogen product had d_4^{20} 0.7995, and its freezing point was −86°.

3-Ethyl-2,2,3-trimethylhexane. The materials taken for the reaction were 28 g of magnesium, 500 ml of absolute ether, 76.6 g of allyl chloride, and 124.2 g of 3-chloro-2,2,3-trimethylpentane [4]. The reaction was carried out by Yarovsky's procedure, the mixture of chloro compounds being added over six hours. The contents of the flask were then heated for 36 hours, and decomposition was effected with 5% HCl. After removal of ether, the residue was fractionated through a column over sodium, and 11 g (9%) of 4-ethyl-4,5,5-trimethyl-1-hexene (b.p. 59° (12 mm); n_D^{20} 1.4403; d_4^{20} 0.7834) was obtained. The olefin was hydrogenated over Raney nickel at 140°, the initial pressure being 130 atm. The hydrogenation product, after distillation through a colunn, had the following properties: b.p. 176.5° (739 mm); n_D^{20} 1.4386; d_4^{20} 0.7783; freezing point −110° (it freezes to a glass).

2,4,4,5,5,7-Hexamethyloctane. 2,4-Dimethyl-2-pentanol was prepared by Konovalov's method [15]. The corresponding chloro compound was then synthesized for the first time by treatment with gaseous HCl at 0°. The yield was 70%, and it had b.p. 52° (46 mm); n_D^{20} 1.4180; d_4^{20} 0.8601.

Found %: Cl 26.72

$C_7H_{15}Cl$. Calculated %: Cl 26.33

The materials taken for the reaction were 11 g of magnesium, 500 ml of absolute ether, and 125.9 g of 2-chloro-2,4-dimethylpentane. Reaction was initiated by the addition of 2 ml of ethyl bromide, and a solution of the chloro compound in ether was then added over six hours. After the addition was complete the contents of the flask were heated at the boiling point of ether for 32 hours. After removal of ether and 2,4-dimethyl-1-pentene by distillation, the residue was fractionated over sodium through a six-plate column. The product was 5.2 g (6%) of 2,4,4,5,5,7-hexamethyloctane, b.p. 216° (743 mm); n_D^{20} 1.4408; d_4^{20} 0.7902; freezing point + 2° (crystals).

Yu. P. Egorov determined the Raman spectrum of the hydrocarbon, which included intensive lines at 697, 936, 1210, and 1236 cm^{-1}. A consideration of Stepanov's calculations [16] and experimental data for $C_{10}-C_{12}$ hydrocarbons having tertiary carbons at the periphery and at the center shows that these lines must be regarded as characterizing the presence of two tertiary carbons in the center of the molecule. The frequencies 823, 960, and 1173 cm^{-1}, characterizing simple branching at the end of the chain, were also found in the spectrum.

It is interesting to note that, as Levina [17] has shown, it is not possible to obtain the above-indicated structure (but in the form of a diolefin) by the condensation of two molecules of the HBr-addition product from 2,4-dimethyl-1,3-pentadiene in presence of sodium; quantitative dehydrobromination to 2,4-dimethyl-1,3-pentadiene occurs, and a dimer of composition $C_{14}H_{24}$ is formed.

SUMMARY

1. It is shown that the use of 2-alkenyl halides or ketones having a α,β-double bond in organomagnesium syntheses gives higher yields than those obtained with saturated halogen compounds or ketones and, moreover, permits the synthesis of compounds that are so greatly branched that they camot be obtained at all when saturated components are used in the synthesis.

2. Halogen compounds of the allyl type that are able to undergo the allyl rearrangement during condensation with saturated ketones do not undergo this change during condensation with α,β-unsaturated ketones (i.e., when there is a conjugated system of bonds in each component).

3. Whereas the condensation of allyl and 2-methylallyl halides with symmetrical saturated tertiary halides containing two adjacent quaternary carbons (2-halo-2,3,3-trimethylbutane) proceeds with low yield, asymmetrical halogen compounds of the same type but of higher molecular weight, in which one of the methyl radicals standing at the carbon attached to the halogen is replaced by propyl or isobutyl, give high yields in the condensation reaction.

Received April 12, 1955

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

LITERATURE CITED

[1] F. Whitemore, A. Homeyer, J. Am. Chem. Soc., 55, 4555 (1933).

[2] G. Edgar, G. Galingaert, R. Marker, J. Am. Chem. Soc., 51, 1483 (1929).

[3] A. L. Liberman and B. A. Kazansky, Proc. Acad. Sci. USSR; 40, 402 (1943).

[4] A. P. Meshcheryakov, E. I. Erzyutova and A. D. Petrov, Proc. Acad. Sci. USSR, 85, 111 (1952).

[5] R. Ya. Levina and S. A. Egorova, J. Gen. Chem., 16, 821 (1946); R. Ya. Levina, A. A. Fainzilberg and N. P. Shusherina, J. Gen. Chem., 20, 868 (1950). [T.p. 903].*

[6] A. D. Petrov, V. I. Koptev and E. P. Kaplan, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1944, No. 2-3, 153.

[7] A. D. Petrov and V. A. Ponomarenko, Proc. Acad. Sci. USSR, 74, 739 (1950).

[8] A. D. Petrov, V. M. Melekhin and V. L. Sushchinsky, Proc. Acad. Sci. USSR, 89, 487 (1953).

[9] A. D. Petrov and M. P. Shebanova, Proc. Acad. Sci. USSR, 84, 721 (1952).

[10] A. D. Petrov and L. N. Lavrishcheva, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 4, 733. [T.p. 631].*

[11] H. Gilman, Organic Chemistry, An Advanced Treatise, 11, 1875.

[12] I. L. Kondakov, J. Russ. Phys. Chem. Soc., 26, 5 (1894).

[13] L. I. Antsus and A. D. Petrov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1950, No. 6, 599.

[14] F. Whitmore, D. Goldsmith, N. Cook, J. Am. Chem. Soc., 72, 53 (1950).

[15] M. Konovalov, J. Russ. Chem. Soc., 37, 910 (1905).

[16] B. I. Stepanov, J. Phys. Chem., 20, 917 (1946).

[17] R. Ya. Levina, Synthesis and Catalytic Transformations of Unsaturated Hydrocarbons, Moscow Univ. Press, 1949, p. 204.

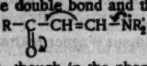
---

* T.p. = Consultants Bureau Translation pagination.

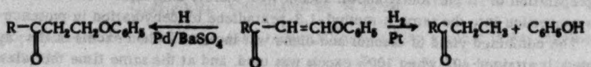
SOME REACTIONS OF ALKYL 2-PHENOXYVINYL KETONES

A. N. Nesmeyanov, N. K. Kochetkov, M. I. Rybinskaya and E. V. Uglova

Alkyl 2-phenoxyvinyl ketones, which were prepared recently in our laboratory by the reaction of alkyl 2-chlorovinyl ketones with phenols [1], have received very little study. The readiness with which the phenoxy group undergoes exchange reactions is of interest: it is eliminated in treatments with acidic reagents and also in the formation of heterocyclic systems from 2-phenoxyvinyl ketones [1]. Apart from these reactions we have studied a peculiar rearrangement of 2-phenoxyvinyl ketones into pyrylium salts which is reminiscent of the Fries rearrangement [2].

The present paper is devoted to the further investigation of the chemical behavior of alkyl 2-phenoxyvinyl ketones. It was considered to be of interest to compare the reactivity of these substances with that of 2-dialkylaminovinyl ketones, which have been recently studied by one of us [3], and also with that of 2-chlorovinyl ketones. It would be expected that, with respect to the activity of the double bond and carbonyl group, 2-phenoxyvinyl ketones would occupy an intermediate position between these other two classes of compound. The conjugation of the free electron pair of the hetero-atom with the double bond and the carbonyl group, to which the deactivation found in aminovinyl ketones is to be attributed  $R-\underset{\underset{O}{\|}}{C}-CH=CH-NR_2$ [3], will obviously be less effective when nitrogen is replaced by the oxygen of the phenoxy group, though in the phenoxyvinyl ketones this conjugation must be more marked than in 2-chlorovinyl ketones. These considerations lead us to suppose that in 2-phenoxyvinyl ketones the carbonyl group and, particularly, the double bond will be less reactive than in 2-chlorovinyl ketones, though this deactivation will not be as great as in 2-dialkylaminovinyl ketones. Our results confirm this view.

We first examined the catalytic hydrogenation of alkyl 2-phenoxyvinyl ketones at room temperature and normal pressure with the object of comparing them with 2-aminovinyl ketones, which are unable to undergo normal hydrogenation [3]. It was found that the hydrogenation of alkyl 2-phenoxyvinyl ketones (the methyl and propyl ketones were used) takes different courses according to which catalyst is used. Over palladium precipitated on barium sulfate the reaction goes normally, and the corresponding alkyl 2-phenoxyethyl ketones are formed in high yield, although it must be pointed out that the process is very slow, the hydrogenation of even very small amounts being complete only after 6-7 hours. On the other hand, hydrogenation over an Adams platinum catalyst does not give the expected reaction product. Instead, hydrogenolysis of the oxygen-carbon bond occurs, and only phenol and the corresponding saturated ketone can be isolated from the reaction mixture:

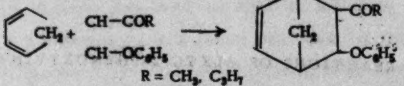


$$R-\underset{\underset{O}{\|}}{C}CH_2CH_2OC_6H_5 \xleftarrow[Pd/BaSO_4]{H} R\underset{\underset{O}{\|}}{C}-CH=CHOC_6H_5 \xrightarrow[Pt]{H_2} R\underset{\underset{O}{\|}}{C}CH_2CH_3 + C_6H_5OH$$

$R = CH_3, C_3H_7$

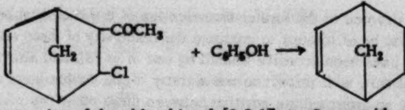
The hydrogenation of alkyl 2-phenoxyvinyl ketones is, therefore, an example of a reaction in which catalysts as similar in character as platinum and palladium give completely different results. The observed behavior shows also that in alkyl 2-phenoxyvinyl ketones the double bond is indeed deactivated (slow hydrogenation over palladium; hydrogenolysis over platinum). This deactivation, however, is not as great as that found in 2-aminovinyl ketones, since the latter, unlike the phenoxy compounds, are unable to undergo normal hydrogenation.

From this point of view the observed behavior of alkyl 2-phenoxyvinyl ketones in a diene-synthesis reaction is particularly characteristic. It is known that 2-chlorovinyl ketones are active dienophiles [4, 5], whereas, owing to the complete deactivation of the double bond, 2-dialkylaminovinyl ketones do not condense with dienes [3]. It was found that neither at room temperature nor at 100° for several hours will methyl or propyl 2-phenoxyvinyl ketone condense with cyclopentadiene, which was selected as one of the most active dienes. This behavior sharply differentiates 2-phenoxyvinyl ketones from 2-chlorovinyl ketones, which react already in the cold with cyclopentadiene [4], forming adducts in high yield. However, under very vigorous conditions (145-155° for 15-16 hours) normal diene condensation occurs with formation of the corresponding phenoxy derivatives of bicyclo[2.2.1]hept-2-ene:



It must be pointed out, however, that under the severe conditions the condensation products are formed in moderate yields (30-50%). The structures of the resulting compounds were confirmed by tests for the double bond and the carbonyl group (formation of a dinitrophenylhydrazone) and by a positive iodoform test.

A confirmatory synthesis was carried out for 5-acetyl-6-phenoxybicyclo[2.2.1]hept-2-ene (methyl 3-phenoxybicyclo[2.2.1]hept-5-en-2-yl ketone), the starting point being 5-acetyl-6-chlorobicyclo[2.2.1]hept-2-ene, which has been prepared previously [4]. As one of us and Karpeisky [6] have shown, the chlorine atom of this compound can readily be replaced by other nucleophilic groups. We found that treatment of 5-acetyl-6-chlorobicyclo[2.2.1]-hept-2-ene with sodium phenoxide in molten phenol or with phenol in an aqueous medium gave a phenoxy derivative in high yield, and the product was found to be identical with the substance obtained by the direct condensation of cyclopentadiene and methyl 2-phenoxyvinyl ketone:

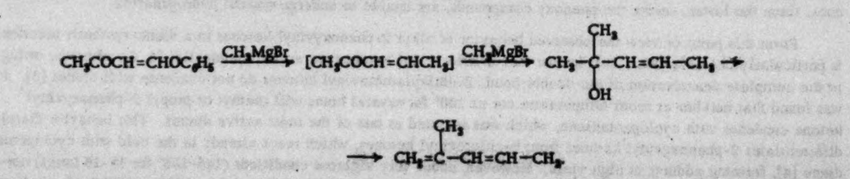


The results obtained for the reaction of the chlorobicyclo[2.2.1]hept-2-ene with phenol are interesting in that they provide final confirmation for the hypothesis advanced previously [6], according to which the replacement of chlorine in this compound occurs without Wagner rearrangement of the carbon skeleton.

Reverting now to the diene condensation of 2-phenoxyvinyl ketones, we must conclude that the results obtained provide particularly clear evidence for the middle place that the double bond of 2-phenoxyvinyl ketones occupies, with respect to activity, in the series: 2-chlorovinyl ketones — 2-phenoxyvinyl ketones — 2-aminovinyl ketones.

In order to elucidate the nature of the carbonyl group in alkyl 2-phenoxyvinyl ketones, it was of interest to determine the behavior of these compounds in reaction with organomagnesium compounds. Investigation showed that reactions of this type are rather complex, and this paper describes only the reaction of methyl 2-phenoxyvinyl ketone with methylmagnesium bromide. Carrying out the reaction under the usual conditions, i.e., by addition of methyl 2-phenoxyvinyl ketone to an equimolecular amount of theorganomagnesium compound, we were able to isolate two substances from the reaction mixture, the total yield being about 20%. One of these substances was the unsaturated alcohol 2-methyl-3-penten-2-ol, and the other the product resulting from the dehydration of this alcohol — 2-methyl-1,3-pentadiene. The structure of the latter was proved not only by the coincidence of constants, but also by the preparation of its previously known adduct with maleic anhydride. The structure of the alcohol was confirmed by its conversion into the same 2-methyl-1,3-pentadiene by dehydration in presence of small amounts of sulfuric acid. The combined yield of alcohol and diene was increased when excess of the organomagnesium compound was used; it attained 40% when 100% excess was used, and at the same time the relative proportion of diene in the mixture increased [7]. The same results were obtained by carrying out the reaction under different conditions — under intense cooling (to −50°) and with reversal of the order of mixing the reactants — but the yields of diene and alcohol were then reduced.

The formation of 2-methyl-3-penten-2-ol, and hence of the diene obtained by its dehydration, can be most readily understood on the assumption that the unsaturated ketone 3-penten-2-one is first formed and then reacts further with the organomagnesium compound to give the unsaturated alcohol:



$$CH_3COCH{=}CHOC_6H_5 \xrightarrow{CH_3MgBr} [CH_3COCH{=}CHCH_3] \xrightarrow{CH_3MgBr} CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}{-}CH{=}CH{-}CH_3 \rightarrow$$

$$\rightarrow CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}CH{=}CH{-}CH_3$$

Hence, the first stage of the reaction is probably the replacement of the phenoxy group, and not condensation at the carbonyl group. We cannot maintain that this is the only direction that reaction takes, for the yield of the isolated substances is only 40% and the residue remaining undistilled is considerable and may contain substances formed by primary reaction at the carbonyl group. It is notable also that 2-chlorovinyl ketones react only at the carbonyl group with organomagnesium compounds [8]. However, the primary reaction of the phenoxyvinyl ketones is replacement of the phenoxy group, which indicates some suppression of the typical properties of the carbonyl group relative to the level found in 2-chlorovinyl ketones.

Thus, the results of catalytic hydrogenation, diene condensation, and reaction with organomagnesium compounds confirm the correctness of the hypothesis advanced at the beginning of the paper concerning the middle place occupied by 2-phenoxyvinyl ketones in the series: 2-chlorovinyl ketones – 2-phenoxyvinyl ketones – 2-aminovinyl ketones.

Finally, we investigated the peculiar reaction of hydrolytic decomposition which 2-phenoxyvinyl ketones undergo in an alkaline medium. It was found that these substances are in no sense inert to the action of aqueous alkalis, a fact which had been indicated indirectly in the course of the development of the method for synthesizing them [1]. When methyl 2-phenoxyvinyl ketone was heated at 30-40° for several hours with 15% aqueous caustic soda, hydrolytic decomposition occurred; acetone and phenol were isolated from the resulting mixture and identified, and a calomel test indicated the presence of formic acid. Similar hydrolytic decomposition is undergone by certain alkoxyvinyl ketones [9]. The occurrence of such decomposition indicates the peculiar character of alkyl phenoxyvinyl ketones, which can be regarded as vinylogs of phenyl esters.

EXPERIMENTAL

1. Hydrogenation of methyl 2-phenoxyvinyl ketone (4-phenoxy-3-buten-2-one) over palladium. Methyl 2-phenoxyvinyl ketone (9.0 g) was hydrogenated in 80 ml of absolute ether over palladium precipitated on barium sulfate (0.5 g of catalyst containing 7% of palladium). In the course of six hours 1.09 liters of hydrogen (calculation requires 1.24 liters) was absorbed, and hydrogenation was discontinued. The catalyst was filtered off, and the filtrate was washed with an alkaline permanganate solution, washed with water, and dried over sodium sulfate. The ether was removed, and the residue was vacuum-distilled. After redistillation methyl 2-phenoxyethyl ketone had the following constants: b.p. 123-124° (8 mm); d_4^{20} 1.0606; n_D^{20} 1.5165; yield 6.6 g (73.3%).

Found %: C 73.24; 73.04; H 7.38; 7.29
$C_{10}H_{12}O_2$. Calculated %: C 73.14; H 7.37

Methyl 2-phenoxyethyl ketone (4-phenoxy-2-butanone) is a colorless liquid of pleasant odor. It is immiscible with water.

Its dinitrophenylhydrazone was prepared in the usual way. After recrystallization from alcohol it was obtained as yellow needles melting at 143-144°.

Found %: N 16.38; 16.39
$C_{16}H_{16}O_5N_4$. Calculated %: N 16.28

Its oxime was prepared in the usual way. After recrystallization from alcohol it was obtained as colorless needles melting at 67-68°.

Found %: N 8.07; 7.85
$C_{10}H_{13}O_2N$. Calculated %: N 7.82.

2. Hydrogenation of 2-phenoxyvinyl propyl ketone (1-phenoxy-1-hexen-3-one) over palladium. The hydrogenation of 7.0 g of 2-phenoxyvinyl propyl ketone was carried out in a similar way (0.4 g of catalyst). In the course of 6.5 hours, 800 ml of hydrogen was absorbed (theory requires 820 ml). Similar treatment yielded 5.0 g (71.4%) of 2-phenoxyethyl propyl ketone, b.p. 126-126.5° (4 mm), which solidified completely. After recrystallization from petroleum ether the substance melted at 36-37.5°.

Found %: C 75.35; 75.36; H 8.32; 8.26
$C_{12}H_{16}O_2$. Calculated %: C 75.00; H 8.39

2-Phenoxyethyl propyl ketone (1-phenoxy-3-hexanone) is soluble in alcohol and ether, but not in water.

3. Hydrogenation of 2-phenoxyvinyl propyl ketone over platinum. 2-Phenoxyvinyl propyl ketone (10.0 g) was hydrogenated in 70 ml of absolute ether over 0.2 g of Adams platinum oxide. In the course of ten hours 2.20 liters of hydrogen was absorbed (theory requires 2.30 liters for two molecular proportions). The catalyst was filtered off, and the filtrate was washed with 10% caustic soda solution, washed with an alkaline permanganate solution, and dried over sodium sulfate. The residue remaining after removal of ether was distilled twice, and a fraction boiling at 120-125° was collected. This fraction was converted into its dinitrophenylhydrazone, which was recrystallized from alcohol as yellow crystals, m.p. 128-129°. It showed no depression in melting point when mixed with the dinitrophenylhydrazone of ethyl propyl ketone (3-hexanone), the reported melting point of which is 130° [10]. The aqueous-alkali extract was acidified with 20% sulfuric acid, and bromine water was added until it was no longer decolorized. The precipitate of tribromophenol was filtered off and recrystallized from alcohol in the form of colorless crystals, m.p. 92-93°, undepressed by admixture of a known sample. The reported melting point of tribromophenol is 94° [11].

4. Condensation of methyl 2-phenoxyvinyl ketone with cyclopentadiene. A mixture of 10 g of methyl 2-phenoxyvinyl ketone and 6.5 g of freshly distilled cyclopentadiene was prepared in an ampoule, which was placed, unsealed, in a small autoclave and heated at 145-155° for 15 hours. The reaction products from three such experiments were combined and vacuum-distilled, the fraction boiling at 132-138° (1.5 mm) being collected. After redistillation, 5-acetyl-6-phenoxybicyclo[2.2.1]hept-2-ene had the following constants: b.p. 132-134° (1.5 mm); d_4^{20} 1.1159; n_D^{20} 1.5481; found MR 64.93; calculated for $C_{15}H_{16}O_2\digamma_4$: MR 64.65; the yield was 13.6 g (29%).

Found %: C 78.61; 78.50; H 7.17; 7.06
$C_{15}H_{16}O_2$. Calculated %: C 78.94; H 7.01

The substance is a yellowish viscous oil having a camphorlike odor. It changes little with keeping.

Its dinitrophenylhydrazone was prepared in the usual way. After recrystallization from glacial acetic acid it formed orange needles, m.p. 152-153°.

Found %: C 62.65; H 5.05
$C_{21}H_{20}O_5N_4$. Calculated %: C 61.72; H 4.90

5. Condensation of 2-phenoxyvinyl propyl ketone with cyclopentadiene. The reaction was carried out under similar conditions with 12 g of 2-phenoxyvinyl propyl ketone and 10 g of cyclopentadiene, two experiments being performed. After two redistillations, 5-butyryl-6-phenoxybicyclo[2.2.1]hept-2-ene had the following constants: b.p. 147-150° (2 mm); d_4^{20} 1.0814; n_D^{20} 1.5370; found MR 73.89; calculated for $C_{17}H_{20}\digamma_4$: MR 73.89; the yield was 15.9 g (49%).

Found %: C 79.56; 79.45; H 7.90; 7.97
$C_{17}H_{20}O_2$. Calculated %: C 79.61; H 7.87

The substance is a yellowish viscous oil having a camphorlike odor. It changes little with keeping.

6. Reaction of 5-acetyl-6-chlorobicyclo[2.2.1]hept-2-ene with phenol. A. To 75 g of melted phenol 1.35 g of sodium was added in small portions, and then 10 g of 5-acetyl-6-chlorobicyclo[2.2.1]hept-2-ene [4] was added gradually. The mixture was shaken for 5.5 hours, heat being applied from time to time. It was then poured into water, and 75 ml of 40% caustic soda was added. The mixture was filtered, and the filtrate was extracted with ether. The extract was washed with 10% caustic soda to remove phenol, and then washed with water and dried over sodium sulfate. Ether was distilled off, and the residue was vacuum-distilled. 5-Acetyl-6-phenoxybicyclo[2.2.1]hept-2-ene has the following constants: b.p. 136-140° (5 mm); d_4^{20} 1.1157; n_D^{20} 1.5471; the yield was 6.45 g (48.9%).

B. 5-Acetyl-6-chlorobicyclo[2.2.1]hept-2-ene (10 g) was added to a solution of 25 g of phenol in 45 ml of 40% caustic potash solution, the mixture being shaken during the addition and then for a further five hours. After the treatment described above (A), 9.6 g (72.2%) of 5-acetyl-6-phenoxybicyclo[2.2.1]hept-2-ene was obtained. It had the following properties: 136-138° (5 mm); d_4^{20} 1.1161; n_D^{20} 1.5477.

The dinitrophenylhydrazones obtained in the usual way from the two samples of 5-acetyl-6-phenoxybicyclo[2.2.1]hept-2-ene both melted at 152-154° after recrystallization from acetic acid. Mixture tests on these two samples and the sample obtained in Experiment 4, taken in pairs, showed no depression.

7. Reaction of methyl 2-phenoxyvinyl ketone with methylmagnesium bromide. A solution of methylmagnesium bromide was prepared in the usual way from 16 g of magnesium and the corresponding amount of methyl bromide in 350 ml of ether. It was placed in a three-necked flask, which was provided with stirrer, reflux condenser, and dropping funnel. Cooling was applied by means of an ice mixture, and 50 ml of a solution of 50 g of methyl 2-phenoxyvinyl ketone in 75 ml of ether was added dropwise. Toward the end of the reaction a white precipitate appeared. The mixture was stirred for one hour and then poured into a mixture of ice and ammonium chloride. The ether layer was separated, and the aqueous layer was extracted with ether. The combined extract was washed with 3% caustic soda solution to remove phenol, and was then washed with water and dried over sodium

sulfate. The ether was carefully distilled off, and the residue was distilled. At 82-90° a substance came over together with water. The water was separated, and the organic layer was dried and redistilled, two fractions being collected: Fraction I, b.p. 74-77° (750 mm), and Fraction II, b.p. 68-72° (128 mm). Redistillation of Fraction I yielded 2-methyl-1,3-pentadiene, the constants of which were: b.p. 74-75° (750 mm); d_4^{20} 0.7209· n_D^{20} 1.4460; the yield was 5.2 g (20%). For 2-methyl-1,3-pentadiene the literature [12] gives b.p. 75.6-76°; d_4^{20} 0.7190; n_D^{20} 1.4466.

Found %: C 87.71; 87.69; H 12.46; 12.31
C_6H_{10}. Calculated %: C 87.80; H 12.20

Redistillation of Fraction II yielded 2-methyl-3-penten-2-ol, which had the following constants: b.p. 121-122°; d_4^{20} 0.8370; n_D^{20} 1.4302; The yield was 6.1 g (19%). For 2-methyl-3-penten-2-ol the literature [12] gives b.p. 121.6-122°; d_4^{20} 1.4295; n_D^{20} 0.8343.

Found %: C 71.62; 71.47; H 12.13; 11.97
$C_6H_{12}O$. Calculated %: C 71.95; H 12.01

After the distillation of Fractions I and II, a thick resinous mass remained in the distillation flask, and from this we could remove only a small amount of phenol by distillation.

8. Reaction of 2-methyl-1,3-pentadiene with maleic anhydride. A mixture of 1.6 g of the diene, 1.9 g of maleic anhydride, and 25 ml of benzene was set aside overnight. Benzene was then removed under reduced pressure, and the residue was washed with hot water. The undissolved crystals were filtered off and recrystallized from ligroin. Colorless plates melting at 55.5-56.5° were obtained. For the adduct formed by 2-methyl-1,3-pentadiene with maleic anhydride the literature [13] gives m.p. 57°.

9. Dehydration of 2-methyl-3-penten-2-ol. A few drops of 40% sulfuric acid were added to 7 g of the alcohol contained in a Favorsky flask, and the mixture was heated gently over a gauze. The distillate separated into two layers, and the water layer was removed. The organic layer was dried over sodium sulfate and distilled, when it yielded 4.7 g (84%) of 2-methyl-1,3-pentadiene, b.p. 75-77°; d_4^{20} 0.7207; n_D^{20} 1.4460.

The adduct with maleic anhydride, prepared as described above, melted at 55-56° and showed no depression of melting point in admixture with the substance obtained in Experiment 8.

10. Reaction of methyl 2-phenoxyvinyl ketone with alkali. Methyl 2-phenoxyvinyl ketone (28 g) was stirred vigorously for 4-5 hours with 170 ml of a 15% solution of caustic soda, the mixture being heated in a water bath maintained at 40-50°. At the end of the reaction the mixture became homogeneous. A fraction boiling at 53-58° was separated from it with the aid of a good fractionating column. After redistillation the substance boiled at 55-57°. It was converted in the usual way into its dinitrophenylhydrazone, which had m.p. 122°, undepressed by admixture of known dinitrophenylhydrazone of acetone, for which the literature [14] gives m.p. 122-124°.

The residue remaining after removal of acetone was acidified with 10% sulfuric acid until feebly acid to litmus, and was then saturated with sodium carbonate. The solution was extracted with ether, the extract was dried over sodium sulfate, and the ether was distilled off. Distillation of the residue yielded 12.8 g (78.7%) of phenol, which was identified by conversion into tribromophenol. To one twenty-fifth part of the alkaline solution a saturated mercuric chloride solution was added. The mixture was brought to the boil and then set aside overnight. The precipitate of calomel was filtered off. The yield was 1.45 g, which corresponds to 0.25 g (80% of the theoretical amount) of formic acid. An ammonia test for calomel was positive.

SUMMARY

1. Hydrogenation of alkyl 2-phenoxyvinyl ketones over a palladium catalyst yields alkyl 2-phenoxyethyl ketones, but in their hydrogenation over a platinum catalyst hydrogenolysis of the carbon-oxygen bond occurs, so that phenol and the corresponding saturated ketone are formed.

2. Reaction of alkyl 2-phenoxyvinyl ketones with cyclopentadiene yields derivatives of bicyclo[2.2.1]hept-2-ene. This reaction, however, goes only under severe conditions, and the yields are not high.

3. Reaction of methyl 2-phenoxyvinyl ketone with methylmagnesium bromide results in the formation of 2-methyl-1,3-pentadiene and 2-methyl-3-penten-2-ol.

4. When methyl 2-phenoxyvinyl ketone is heated with aqueous alkali, it undergoes hydrolytic decomposition to acetone, phenol and formic acid.

5. The results indicate that, with respect to the reactivities of the double bond and carbonyl group, 2-phenoxyvinyl ketones occupy an intermediate position between 2-chlorovinyl ketones and 2-aminovinyl ketones.

Received September 15, 1954

M. V. Lomonosov Moscow State University

LITERATURE CITED

[1] N. K. Kochetkov, M. I. Rybinskaya, and A. N. Nesmeyanov, Proc. Acad. Sci. USSR, 79, 799 (1951).

[2] A. N. Nesmeyanov, N. K. Kochetkov and M. I. Rybinskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 3, 418. [T.p. 353].*

[3] N. K. Kochetkov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 1, 47. [T.p. 37].*

[4] A. N. Nesmeyanov, N. K. Kochetkov, M. Ya. Karpeisky, and G. V. Aleksandrova, Proc. Acad. Sci. USSR, 82, 409 (1952).

[5] N. K. Kochetkov and G. V. Aleksandrova, Proc. Acad. Sci. USSR, 85, 1033 (1952).

[6] N. K. Kochetkov and M. Ya. Karpeisky, Proc. Acad. Sci. USSR, 85, 801 (1952).

[7] A. Klages, Ber., 35, 2633 (1902).

[8] M. Julia, Ann. chim. [10], 5, 595 (1950).

[9] W. Johnson, H. Posvic, J. Am. Chem. Soc., 69, 1361 (1947).

[10] C. Allen, J. Am Chem. Soc., 52, 2955 (1930).

[11] F. Körner, Ann., 137, 203 (1866).

[12] V. Keersbilck, Bull. Soc. Chim. Belg., 38, 207 (1929).

[13] C. Bachmann, J. Am. Chem. Soc., 64, 787 (1942).

[14] W. Dischert, H. Nahm, Ber., 73, 448 (1940).

---

* T.p. = Consultants Bureau Translation pagination.

SYNTHESIS OF DODECANEDIOIC AND HEXADECANEDIOIC ACIDS

A. N. Nesmeyanov, L. I. Zakharkin and T. A. Kost

$\alpha,\alpha,\alpha,\omega$-Tetrachloroalkanes $Cl(CH_2)_nCCl_3$ are of interest for the synthesis of α,ω-bifunctional compounds on account of the possibility of applying the reductive dimerization reaction given by the CCl_3 group:

$$2RCCl_3 + H_2 \rightarrow RCCl_2CCl_2R + 2HCl$$

and of then reducing the CCl_2CCl_2 grouping. The reductive dimerization of the CCl_3 group has been studied in detail for benzotrichloride [1] and 2,2-diaryl-1,1,1-trichloroethanes [2, 3, 4]. For the preparation of compounds of this type reduction has been effected electrochemically, by the action of reducing agents of the Devarda type, and catalytically with Pt and Pd catalysts in presence of bases. The reductive dimerization of $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes over a platinum catalyst (prepared from PtO_2) in presence of ammonia is described in a patent [5], and it is stated that reduction can be carried out further with the formation of dimeric α,ω-dichloroalkanes:

$$Cl(CH_2)_nCCl_3 \rightarrow [Cl(CH_2)_nCCl_2]_2 \rightarrow Cl(CH_2)_{2n+2}Cl.$$

The selective action of hydrogen in this reaction, in which it preferentially attacks a CCl_3 group in presence of a CH_2Cl group, is in accord with the view that we have advanced previously, namely that the action of reagents of the radical type on tetrachloroalkanes should be directed, in the first place, to the CCl_3 group [6].*

The ready accessibility of 1,1,1,5-tetrachloropentane and 1,1,1,7-tetrachloroheptane makes it possible to use the compounds obtained by this reaction for the synthesis of the comparatively difficultly accessible dodecanedioic and hexadecanedioic acids. With this object we have made a more detailed investigation of the reductive dimerization of 1,1,1,5-tetrachloropentane and 1,1,1,7-tetrachloroheptane and of the further reduction of the products.

The reduction of tetrachloroalkanes to α,ω-dichloroalkanes proceeds in stages: after the formation of a dimeric hexachloroalkane, dechlorination occurs with formation of a dimeric tetrachloroalkene, which is then reduced to the α,ω-dichloroalkane:

$$Cl(CH_2)_nCCl_3 \rightarrow [Cl(CH_2)_nCCl_2]_2 \rightarrow [Cl(CH_2)_nCCl=]_2 \rightarrow Cl(CH_2)_{2n+2}Cl.$$

An interesting feature is the great ease with which the grouping $-CCl=CCl-$ reduces, as compared with CH_2Cl.

Hence, by the reduction of 1,1,1,5-tetrachloropentane, 1,5,5,6,6,10-hexachlorodecane, 1,5,6,10-tetrachloro-5-decene, and 1,10-dichlorodecane can be prepared, and by the reduction of 1,1,1,7-tetrachloroheptane, 1,7,7,8,8,14-hexachlorotetradecane, 1,7,8,14-tetrachloro-7-tetradecene, and 1,14-dichlorotetradecane can be prepared.

We have observed also another example of dechlorination during the catalytic hydrogenation of such polychloro compounds: in the hydrogenation of 1,1,1,2,5-pentachloropentane there is no dimerization with formation of $[Cl(CH_2)_3CHClCCl_2]_2$, but dechlorination occurs with formation of 1,1,5-trichloro-1-pentene.

When 1,1,1,5-tetrachloropentane and 1,1,1,7-tetrachloroheptane are hydrogenated over a platinum catalyst (prepared from PtO_2) or 5% $Pd/BaSO_4$ in presence of one equivalent of ammonia, similar results are obtained: hexachlorodecane and hexachlorotetradecane are obtained in yields varying around 50%, and at the same time considerable amounts of 1,1,5-trichloropentane and 1,1,7-trichloroheptane are obtained, i.e., hydrogenation proceeds in both possible directions:

---

* In this connection attention must be drawn to the incorrectness of a statement made in an American patent [7], namely that 1,1,1,6,6,6-hexachlorohexane results from the action of certain metals on 1,1,1,3-tetrachloropropane. The constants of this compound coincide with those of 1,3,3,4,4,6-hexachlorohexane, which we prepared by the action of Raney nickel on 1,1,3-tetrachloropropane.

$$Cl(CH_2)_nCCl_3 \xrightarrow[Pt,\ Pd]{H_2} [Cl(CH_2)_nCCl_2]_2 + Cl(CH_2)_nCHCl_2.$$

$$n = 4 \text{ or } 6$$

When tetrachloropentane and tetrachloroheptane are hydrogenated in presence of two equivalents of ammonia, tetrachlorodecene and tetrachlorotetradecene, respectively, are obtained in 40-45% yield. The direct hydrogenation of tetrachloropentane and tetrachloroheptane to the corresponding α,ω-duchloroalkanes without the isolation of intermediate products proceeds very slowly in the last stage and does not go to completion. Hydrogenation of tetrachloropentane with Raney nickel in presence of aqueous or alcoholic ammonia at atmospheric pressure gives hexachlorodecane in a yield of only 7-9%, but when the reaction is carried out in presence of aqueous alkali at 60-80° the yield of hexachlorodecane is increased to 25-30%. When tetrachloropentane is hydrogenated over Raney nickel in presence of pyridine at 100 atm, no hexachlorodecane is formed, the main product being 1,1,5-trichloropentane. When tetrachloropentane is heated in alcoholic solution with a large amount of Raney nickel without passage of hydrogen, hexachlorodecane is formed.

The hydrogenation of hexachlorodecane and of hexachlorotetradecane over Pt and Pd catalysts in presence of two molecular equivalents of ammonia proceeds readily, and tetrachlorodecene and tetrachlorotetradecene are formed in high yield. Both of the latter compounds are readily formed from the corresponding hexachloroalkanes when these are treated with zinc dust in alcoholic solution:

$$[Cl(CH_2)_nCCl_2]_2 \xrightarrow{Zn} [Cl(CH_2)_nCCl=]_2.$$

The structure of 1,5,6,10-tetrachloro-5-decene was confirmed by its ozonization to 5-chlorovaleric acid.

The hydrogenation of hexachlorodecane to 1,10-dichlorodecane over a Pt catalyst in presence of ammonia is very slow, and the reaction products include a large amount of tetrachlorodecene. Under these conditions, tetrachlorodecene and tetrachlorotetradecene are also hydrogenated very slowly. The hydrogenation of hexachloroalkanes and tetrachloroalkenes to α,ω-dichloroalkanes over $Pd/BaSO_4$ in presence of ammonia or diethylamine proceeds comparatively rapidly and in high yield.

The hydrogenation of hexachlorodecane over Raney nickel in presence of diethylamine at high temperatures and pressures gives dichlorodecane in 70% yield; with ammonia the reaction goes poorly. It follows from our results that for the synthesis of dichlorodecane or dichlorotetradecane from the corresponding tetrachloroalkane the reduction must be carried out in two stages: first to a hexachloro or tetrachloro compound, and then the reduction of these to the α,ω-dichloroalkane. In view of the necessity for two-stage reduction, we consider that the best route for the synthesis of dodecanedioic and tetradecanedioic acids will be the following:

$$[Cl(CH_2)_nCCl=]_2 + 2NaCN \rightarrow [NC(CH_2)_nCCl=]_2 \xrightarrow[H^+]{H_2O} [HOOC(CH_2)_nCCl=]_2 \xrightarrow[Ni]{H_2} HOOC(CH_2)_{2n+2}COOH.$$

The reaction of sodium cyanide with tetrachlorodecene and with tetrachlorotetradecene proceeds smoothly in 2-ethoxyethanol solution; under the conditions of the reaction, the chlorine atoms at the double bond do not react with sodium cyanide. Nitriles obtained in this way were hydrolyzed by heating them with a mixture of hydrochloric and acetic acids, and the dicarboxylic acids formed were hydrogenated at high temperature and pressure in an aqueous alkaline medium in presence of Raney nickel, when dodecanedioic and hexadecanedioic acids were formed. 8,9-Dichloro-8-hexadecenedinitrile was reduced over $Pd/BaSO_4$ in presence of diethylamine and gave hexadecanedinitrile in good yield:

$$[NC(CH_2)_6CCl=]_2 \xrightarrow{H_2} NC(CH_2)_{14}CN$$

When hexachlorodecane was treated with sodium cyanide, only the terminal chlorine atoms reacted. The resulting 6,6,7,7-tetrachlorododecanedinitrile was hydrolyzed into the corresponding tetrachloro acid:

$$[Cl(CH_2)_4CCl_2]_2 \rightarrow [NC(CH_2)_4CCl_2]_2 \rightarrow [HOOC(CH_2)_4CCl_2]_2$$

The corresponding nitriles were prepared also from 1,10-dichlorodecane and 1,14-dichlorotetradecane, and it was found that excellent results were obtained when 2-ethoxyethanol was used as solvent.

EXPERIMENTAL

Hydrogenation of 1,1,1,5-Tetrachloropentane to 1,5,5,6,6,10-Hexachlorodecane

a) 1,1,1,5-Tetrachloropentane (500 g) and 794 ml of a solution of ammonia in ethanol containing 50 g of ammonia were added to previously reduced platinum oxide (2.38 g of platinum oxide in 320 ml of alcohol and 10 ml of glacial acetic acid). Reduction was carried out at atmospheric pressure; it proceeded with evolution of heat. In the course of nine hours 35 liters of hydrogen was absorbed. The reaction mixture was diluted with water until the ammonium chloride was dissolved, and it was then filtered. The precipitate of 1,5,5,6,6,10-hexachlorodecane was dissolved in chloroform, and the solution was dried over calcium chloride. The solvent was removed, and low-boiling substances (180 g) were removed under reduced pressure. The hexachlorodecane, which remained behind, was recrystallized from alcohol. The product was 202 g (48.5%) of hexachlorodecane, m.p. 84-85°.

Fractionation of the low-boiling products through a column yielded 50 g of the original 1,1,1,5-tetrachloro pentane and 105 g of 1,1,5-trichloropentane, b.p. 84° (8 mm); n_D^{20} 1.4788; d_4^{20} 1.2438; found MR 39.93; calculated MR 39.89.

Found %: C 34.30; 34.18; H 5.17; 5.30
$C_5H_9Cl_3$. Calculated %: C 34.18; H 5.12

b) A mixture consisting of 100 g of 1,1,1,5-tetrachloropentane, a solution of 19 g of caustic soda in 50 ml of water, and 3 g of Raney nickel was shaken at 60-90° until hydrogen ceased to be absorbed (12 hours). The product was extracted with chloroform. The chloroform was removed, and the low-boiling part was distilled off under reduced pressure (54.7 g). The amount of 1,5,5,6,6,10-hexachlorodecane obtained was 21.1 g (25.4%).

c) Raney nickel (10 g) was added gradually to a solution of 21 g of tetrachloropentane in 50 ml of alcohol; much heat was evolved. The mixture was boiled for two hours, the catalyst was filtered off, and the oil present was extracted with chloroform. The low-boiling products were distilled off, and 3.5 g (20%) of 1,5,5,6,6,10-hexachlorodecane was obtained. It melted at 83-84°.

Hydrogenation of 1,1,1,7-Tetrachloroheptane to 1,7,7,8,8,14-Hexachlorotetradecane

1,1,1,7-Tetrachloroheptane (83 g) and a solution of 8 g of ammonia in 80 ml of methanol were added to previously reduced 5% Pd/$BaSO_4$ (2 g) in 25 ml of methanol and 1 ml of glacial acetic acid. During the hydrogenation the reaction mixture became warm. After three hours, when 6.1 liters of hydrogen had been absorbed, the absorption of hydrogen ceased. The methanolic solution was filtered from the catalyst and ammonium chloride, and the precipitate was washed with chloroform on the filter. Water was added to the filtrate. The chloroform layer was dried over calcium chloride. After removal of chloroform under reduced pressure, the low-boiling products were distilled off (28 g). Recrystallization of the residue from ethanol yielded 32.1 g (45.5%) of 1,7,7,8,8,14-hexachlorotetradecane, m.p. 57-58°. Fractionation of the low-boiling products through a column yielded 16 g of 1,1,7-trichloroheptane, b.p. 74-75 (1.5 mm); n_D^{20} 1.4776; d_4^{20} 1.1744; found MR 49.13, calculated MR 49.13.

Found %: C 41.08; 41.12; H 6.19; 6.34
$C_7H_{13}Cl_3$. Calculated %: C 41.24; H 6.38

Hydrogenation of 1,1,1,5-Tetrachloropentane to 1,1,5-Trichloropentane

A mixture of 63 g of tetrachloropentane, 25 g of pyridine, and 80 ml of methanol was treated with hydrogen at 100 atm in presence of 5 g of Raney nickel at room temperature. The catalyst was filtered off, and the filtrate was diluted with water and extracted with chloroform. The extract was washed with dilute hydrochlorid acid. After removal of chloroform, the residue was fractionated through a column and yielded 42 g (80%) of 1,1,5-trichloropentane.

Hydrogenation of 1,1,1,5-Tetrachloropentane to 1,5,6,10-Tetrachloro-5-decene

Tetrachloropentane (63 g) was hydrogenated in presence of 0.2 g of PtO_2 and 5.5 g of ammonia in 80 ml of methanol for 2 hours 30 minutes, in the course of which 5.2 liters of hydrogen was absorbed. The mixture was then cooled, and 5.2 g of ammonia was passed in. In the course of further hydrogenation for two hours, a further 5.6 liters of hydrogen was absorbed. The usual treatment yielded 19.2 g (45.5%) of 1,5,6,10-tetrachloro-5-decene, b.p. 152-154° (3 mm); n_D^{20} 1.5055; d_4^{20} 1.2202; found MR 67.56; calculated MR 67.38.

Found %: C 43.37; 43.41; H 5.91; 6.21
$C_{10}H_{16}Cl_4$. Calculated %: C 43.16; H 5.75

Action of Zinc on 1,5,5,6,6,10-Hexachlorodecane

A stirred mixture of 50 g of 1,5,5,6,6,10-hexachlorodecane, 20 g of zinc dust, and 150 ml of ethanol was boiled for six hours. Chloroform was added to the reaction mixture and the zinc was filtered off. Water and a little concentrated hydrochloric acid were added to the filtrate. The chloroform solution was dried over calcium chloride. Vacuum distillation yielded 37.2 g (95%) of 1,5,6,10-tetrachloro-5-decene.

Ozonization of 1,5,6,10-Tetrachloro-5-decene

A solution of 5 g of 1,5,6,10-tetrachloro-5-decene in 60 ml of dry chloroform was treated with 6% ozone for six hours. The reaction mixture was diluted with water, heated for a time at 50-60°, and then boiled for 5-6 hours. The mixture was extracted with chloroform. After removal of solvent, 1.5 g of 5-chlorovaleric acid was isolated and was identified in the form of its anilide, which showed no melting point depression in admixture with known 5-chlorovaleranilide.

Hydrogenation of 1,1,1,7-Tetrachloroheptane to 1,7,8,14-Tetrachloro-7-tetradecene

Tetrachloroheptane (90 g) was hydrogenated in presence of 1.5 g of $Pd/BaSO_4$ and 8.3 g of ammonia in 100 ml of methanol for three hours, in the course of which six liters of hydrogen was absorbed. The reaction mixture was cooled, and 8.1 g of ammonia was passed in. During further hydrogenation for three hours, a further 7.5 liters of hydrogen was absorbed. The usual treatment yielded 28 g (44%) of 1,7,8,14-tetrachloro-7-tetradecene, b.p. 178-180° (2 mm); n_D^{20} 1.4980; d_4^{20} 1.1393; found MR 85.94; calculated MR 85.85.

Found %: C 50.18; 50.07; H 7.40; 7.29

$C_{14}H_{24}Cl_4$. Calculated %: C 50.29; H 7.20

Action of Zinc on 1,7,7,8,8,14-Hexachlorotetradecane

Hexachlorotetradecane (15 g) was added gradually to a stirred mixture of 5 g of zinc dust (previously activated by heating it with 0.1 ml of glacial acetic acid and 0.1 ml of hydrobromic acid) and 30 ml of absolute alcohol. Reaction proceeded with evolution of much heat. After the mixture had been heated for one hour and cooled, chloroform was added. The excess of zinc was filtered off, and dilute hydrochloric acid was added to the filtrate. The chloroform layer was separated, washed with water, and dried with calcium chloride. Vacuum distillation yielded 11.5 g (92%) of 1,7,8,14-tetrachloro-7-tetradecene.

Hydrogenation of 1,7,7,8,8,14-Hexachlorotetradecane to 1,7,8,14-Tetrachloro-7-tetradecene

Hexachlorotetradecane (20 g) was hydrogenated in presence of 1 g of $Pd/BaSO_4$ and 1.8 g of ammonia in 50 ml of methanol for two hours, in the course of which 1.2 liters of hydrogen was absorbed. The usual treatment yielded 13.6 g (81%) of tetrachlorotetradecene.

1,10-Dichlorodecane

a) Tetrachlorodecene (15 g) was hydrogenated in presence of 1 g of $Pd/BaSO_4$ and 2.3 g of ammonia in 70 ml of methanol for five hours, in the course of which 3.6 liters of hydrogen was absorbed. Fractionation of the products yielded 7.6 g (67%) of 1,10-dichlorodecane, b.p. 105-106° (1.5 mm); n_D^{20} 1.4620; d_4^{20} 0.9992; found MR 58.05; calculated MR 58.11. The literature [8] gives b.p. 147-148° (11 mm); d_4^{20} 0.9940.

b) A mixture of 100 g of 1,5,5,6,6,10-hexachlorodecane, 100 g of diethylamine, 200 ml of ethanol, and 12 g of Raney nickel was placed in a one-liter rotating autoclave. Hydrogen was passed into the autoclave until the pressure attained 100 atm. The reaction was carried out at 50-55°, hydrogen being passed in as necessary so that the pressure was maintained at 100-120 atm. After eight hours reaction ceased. The products obtained were 41 g (68%) of 1,10-dichlorodecane and 15 g (19%) of 1,5,6,10-tetrachlorodecene.

1,14-Dichlorotetradecane

a) Tetrachlorotetradecene (28 g) was hydrogenated in presence of 2 g of $Pd/BaSO_4$ and 13 g of diethylamine in 70 ml of methanol for five hours, in the course of which 3.7 liters of hydrogen was absorbed. Dichlorotetradecane is of low solubility in methanol and was to be found mainly in the precipitate. The product was 15.1 g (67%) of 1,14-dichlorotetradecane, b.p. 143-144° (1.5 mm); m.p. 38-39° (from methanol).

Found %: C 63.06; 63.13; H 10.20; 10.44

$C_{14}H_{28}Cl_2$. Calculated %: C 62.92; H 10.48

Reduction was slower in presence of ammonia.

b) Tetrachloroheptane (90 g) was hydrogenated in presence of 1.5 g of Pd/$BaSO_4$ and 8.1 g of ammonia in 100 ml of methanol for 2 hours 30 minutes, in the course of which 7.5 liters of hydrogen was abosrbed. The catalyst and ammonium chloride were filtered off, methanol was distilled off, and low-boiling fractions were removed under reduced pressure. The residue (42 g) was hydrogenated in presence of 3 g of Pd/$BaSO_4$ and 32 g of diethylamine in 80 ml of ethanol for ten hours. The product was 14.5 g (28%) of 1,14-dichlorotetradecane, b.p. 144-146° (1.5 mm), together with about 5 g of a mixture boiling at 150-180° (1 mm) and consisting mainly of tetrachlorotetradecene.

Hydrogenation of 1,1,1,2,5-Pentachloropentane

Pentachloropentane (20 g) and 39 ml of a solution of ammonia in ethanol containing 19.5 g of ammonia were added to previously reduced platinum oxide (0.18 g of PtO_2 in 15.0 ml of ethanol and 0.8 ml of glacial acetic acid). The mixture was shaken with hydrogen for two hours, in the course of which 4 liters of hydrogen was absorbed. The usual treatment and vacuum distillation yielded 4.5 g of the original compound and 8 g (74%) of 1,1,5-trichloro-1-pentene, b.p. 72-74° (10 mm); n_D^{20} 1.4902; d_4^{20} 1.2734. The literature [9] gives b.p. 68-69° (7 mm); n_D^{20} 1.4892; d_4^{20} 1.2724.

6,7-Dichloro-6-dodecenedinitrile

A stirred mixture of 20 g of tetrachlorodecene, 11 g of sodium cyanide, 1 g of sodium iodide, 5 ml of water and 40 ml of 2-ethoxyethanol was heated at 102-106° for four hours. The mixture was cooled, diluted with water, and extracted with chloroform. Vacuum distillation yielded 16.5 g (88%) of 6,7-dichloro-6-dodecenedinitrile, b.p. 212-214° (45 mm); n_D^{20} 1.4943; d_4^{20} 1.1295; found, MR 66.80; calculated, MR 66.52.

Found %: N 10.77; 10.73

$C_{12}H_{16}Cl_2N_2$. Calculated %: N 10.81.

8,9-Dichloro-8-hexadecenedinitrile

A stirred mixture of 32 g of tetrachlorotetradecene, 12 g of sodium cyanide, 0.5 g of sodium iodide, 5 ml of water, and 60 ml of 2-ethoxyethanol was heated at 102-106° for six hours. The mixture was cooled, diluted with water, and extracted with chloroform. Vacuum distillation yielded 26 g (86%) of 8,9-dichloro-8-hexadecenedinitrile, b.p. 212-213°; n_D^{20} 1.4895; d_4^{20} 1.0704; found MR 85.01; calculated MR 85.00.

Found %: N 8.56; 8.58

$C_{16}H_{24}Cl_2N$. Calculated %: N 8.89

6,7-Dichloro-6-dodecenedioic Acid

A solution containing 14.5 g of 6,7-dichloro-6-dodecenedinitrile, 60 ml of glacial acetic acid, 35 ml of concentrated hydrochloric acid, and 18 ml of water was boiled for 15 hours. Addition of water and cooling yielded a precipitate of the acid, amounting to 15.3 g (92%); m.p. 108.5-109.5° (from benzene).

Found %: C 48.66, 48.86; H 6.16, 6.18

$C_{12}H_{18}Cl_2O_4$. Calculated %: C 48.48; H 6.06

8,9-Dichloro-8-hexadecenedioic Acid

Dichlorohexadecenedinitrile (6.5 g) was hydrolyzed by heating it with a mixture of 30 ml of glacial acetic acid, 15 ml of concentrated hydrochloric acid, and 8 ml of water for 20 hours. The yield of acid was 6.8 g (94%), m.p. 95-96° (from benzene).

Found %: C 54.52, 54.58; H 7.10, 7.24

$C_{16}H_{26}Cl_2O_4$. Calculated %: C 54.39; H 7.36

Dodecanedioic Acid

Dichlorododecenedioic acid (10.2 g) was dissolved in aqueous alkali (8 g of caustic soda in 80 ml of water) and hydrogenated in presence of 3 g of nickel catalyst at 60-70° and 100 atm for two hours. The catalyst was filtered off, and thefiltrate was acidified with hydrochloric acid, when 7.3 g (92%) of dodecanedioic acid was obtained. Hexadecanedioic acid was prepared similarly from dichlorohexadecenedioic acid in 93% yield.

Hexadecanedinitrile

Dichlorododecenedinitrile (12 g) was hydrogenated in presence of 1.5 g of $Pd/BaSO_4$ and 10 g of diethylamine in 60 ml of methanol for 90 minutes, in the course of which 2.7 liters of hydrogen was absorbed. The catalyst was filtered off, and the filtrate was diluted with water, acidified with hydrochloric acid, and extracted with benzene. The residue remaining after removal of benzene crystallized out, and 9.1 g of hexadecanedinitrile, m.p. 48-49° (from a mixture of petroleum ether and benzene), was obtained.

Found %: N 11.12, 11.18

$C_{16}H_{28}N_2$. Calculated %: N 11.29

6,6,7,7-Tetrachlorododecanedioic Acid

A stirred mixture of 20 g of 1,5,5,6,6,10-hexachlorodecane, 150 ml of 2-ethoxyethanol, and 5 g of sodium cyanide was heated at 110° for five hours. The mixture was cooled, and the precipitate present was filtered off and washed with water. The yield of crude tetrachlorododecanedinitrile was 12.2 g. A mixture of 10 g of the dinitrile, 20 ml of glacial acetic acid, and 40 ml of hydrochloric acid (1:1) was boiled for 12 hours. The precipitate that formed was filtered off and treated with hot alkali. Treatment of the sodium salt with hydrochloric acid yielded 9 g (80.8%) of 6,6,7,7-tetrachlorododecanedioic acid, m.p. 223° (from ethanol).

Found %: C 39.71, 39,52; H 4.97, 4.97; Cl 38.46; 38.67

$C_{10}H_{10}O_4Cl_4$. Calculated %: C 39.13; H 4.92; Cl 38.58

Dodecanedinitrile

A stirred mixture of 11 g of 1,10-dichlorodecane, 7.5 g of sodium cyanide, 0.5 g of sodium iodide, 5 ml of water, and 25 ml of 2-ethoxyethanol was heated for four hours. The product was 9.3 g (92%) of dodecanedinitrile, b.p. 156-157° (2 mm). In a similar way, hexadecanedinitrile was prepared from 1,14-dichlorotetradecane in a 90% yield.

SUMMARY

1. Dodecanedioic and hexadecanedioic acids were synthesized from 1,1,1,5-tetrachloropentane and 1,1,1,7-tetrachloroheptane respectively.

2. The reductive dimerization of 1,1,1,5-tetrachloropentane and 1,1,1,7-tetrachloroheptane was investigated. It was found that platinum and palladium catalysts give better results than Raney nickel under the conditions studied.

3. It was shown that the reduction of $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes to dimeric α,ω-dichloroalkanes passes through the stage of unsaturated tetrachloro compounds containing the $-CCl{=}CCl$ grouping, which is more readily reduced than the CH_2Cl group.

Received July 24, 1954

Institute of Heteroorganic Compounds of
The USSR Academy of Sciences

LITERATURE CITED

[1] W. Borche, G. Heimburgen, Ber., 48, 452, 850 (1915).

[2] K. Brand, Ber., 54, 1987 (1921).

[3] K. Brand, J. Kerscher, Ber., 54, 2007 (1921).

[4] K. Brand, M. Matshi, Ber., 46, 2942 (1913).

[5] British Patent 652,768; Chem. Abs., 46, 1577c (1952).

[6] A. N. Nesmeyanov, R. Kh. Freidlina, and L. I. Zakharkin, Proc. Acad. Sci. USSR, 96, No. 1, 87 (1954).

[7] U. S. Patent 2,519,691; Chem. Abs., 45, 635c (1951).

[8] S. Kawai, T. Hosono, J Shikinani, S. Jonechi, Sci. Papers, Inst. Phys.-Chem. Research (Tokyo) Nas., 306, 19 (1931); C. 1931, II, 1694.

[9] A. N. Nesmeaynov and L. I. Zakharkin, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 6, 988 (T.p.861)*.

---

* T.p = Consultants Bureau Translation pagination.

DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 8. BISDIALKYLAMIDES OF 2-ALKOXY- AND 2-PHENOXY-VINYLPHOSPHONIC ACIDS

K. N. Anisimov, N. E. Kolobova and A. N. Nesmeyanov

Amides of alkyl- and aryl-phosphonic acids have been prepared by numerous investigators [1-7] by the reaction of alkyl- and aryl-phosphonic dichlorides with amines or their hydrochlorides:

$$RPOCl_2 + 4R_2NH = RPO(NR_2)_2 + 2R_2NH \cdot HCl;$$

$$RPOCl_2 + 2R_2NH \cdot HCl = RPO(NR_2)_2 + 4HCl.$$

There are no data relating to amides of unsaturated phosphonic acids in the scientific literature, but there is an isolated reference to the compound $CH_2=C(CH_3)PO[N(CH_3)_2]_2$ in the patent literature [8]. As we could readily prepare 2-alkoxy- and 2-phenoxy-vinylphosphonic dichlorides by the method that we have developed [9], we synthesized some bisdialkylamides of 2-alkoxy- and 2-phenoxy-vinylphosphonic acids by reaction between one molecule of the acid chloride and four molecules of the secondary amine in an inert solvent.

The bisdialkylamides of 2-alkoxy- and 2-phenoxy-vinylphosphonic acids are viscous liquids that are readily distilled under reduced pressure and are stable to storage. They were obtained in yields of up to 80%. The formulas of the compounds prepared are given with their physical properties in the table.

TABLE

Formula	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}
$C_2H_5-O-CH=CHPO[N(CH_3)_2]_2$	108 (1)	1.4780	1.0401
$i\text{-}C_3H_7-O-CH=CHPO[N(CH_3)_2]_2$	105.5 (2)	1.4742	1.0182
$n\text{-}C_4H_9-O-CH=CHPO[N(CH_3)_2]_2$	116 (1)	1.4755	1.0090
$C_6H_5-O-CH=CHPO[N(CH_3)_2]_2$	145 (2)	1.4858	1.1199
$C_2H_5-O-CH=CHPO[N(C_2H_5)_2]_2$	126.5 (2)	1.4755	1.0950
$i\text{-}C_3H_7-O-CH=CHPO[N(C_2H_5)_2]_2$	132 (2)	1.4709	0.9962
$n\text{-}C_4H_9-O-CH=CHPO[N(C_2H_5)_2]_2$	130 (2)	1.4729	0.9745
$C_6H_5-O-CH=CHPO[N(C_2H_5)_2]_2$	161 (2)	1.5200	1.0402
$C_2H_5-O-CH=CHPO[N(C_4H_9\text{-}n)_2]_2$	172 (2)	1.4680	0.9399
$n\text{-}C_3H_7-O-CH=CHPO[N(C_4H_9\text{-}n)_2]_2$	172 (2)	1.4678	0.9301
$(CH_3)_2-CH-CH_2-CH_2-O-CH=CHPO[N(C_4H_9\text{-}n)_2]_2$	192-193 (2)	1.4691	0.9249
$C_6H_5-O-CH=CHPO[N(C_4H_9\text{-}n)_2]_2$	212 (0.5)	1.5060	0.9886
$C_2H_5-O-CH=CHPO[NC_5H_{10}]_2$	m.p. 60-61		
$C_6H_5-O-CH=CHPO[NC_5H_{10}]_2$	202 (1)	1.5528	1.1193

EXPERIMENTAL

Bisdimethylamide of 2-ethoxyvinylphosphonic acid $C_2H_5-O-CH=CHPO[N(CH_3)_2]_2$. 2-Ethoxyvinylphosphonic dichloride (9.45 g) was added to a well-cooled, stirred mixture of 100 ml of petroleum ether and 9 g of dimethylamine contained in a three-necked flask fitted with stirrer, reflux condenser and dropping funnel. When the whole of the acid chloride had been added, stirring was continued for two hours. The mixture was set aside overnight and then heated at 55-60° in a water bath for two hours. The precipitate of dimethylamine hydrochloride was filtered off and washed three times with petroleum ether. The filtrate was then treated with a saturated solution of caustic soda and dried over calcined potassium carbonate. Petroleum ether and benzene were distilled off, and the residue was left in the boiling water bath for 30 minutes and then vacuum-distilled. Three fractionations yielded 6.4 g (57%) of a substance of b.p. 108° (1 mm); n_D^{20} 1.4780; d_4^{20} 1.0401.

Found %: N 13.54, 13.26
$C_8H_{19}O_2PN_2$. Calculated %: N 13.59

Bisdiethylamide of 2-ethoxyvinylphosphonic acid $C_2H_5-O-CH=CHPO[N(C_2H_5)_2]_2$. 2-Ethoxyvinylphosphonic dichloride (10 g) was added from a dropping funnel to a cooled, stirred mixture of 100 ml of petroleum ether and 17 g of diethylamine. The reaction mixture was then treated as described above, and three fractionations yielded 8 g (59%) of a substance of b.p. 126.5° (1.5 mm); n_D^{20} 1.4755; d_4^{20} 0.0950.

Found %: N 10.37, 10.26
$C_{12}H_{27}O_2PN_2$. Calculated %: N 10.68

Bisdibutylamide of 2-ethoxyvinylphosphonic acid $C_2H_5-O-CH=CHPO[N(C_4H_9\text{-}n)_2]_2$. 2-Ethoxyvinylphosphonic dichloride (9.5 g) was added to a mixture of 28 g of dibutylamine and 130 ml of petroleum ether. Fractionation yielded 12 g of the bisdibutylamide of 2-ethoxyvinylphosphonic acid, b.p. 172° (2 mm); n_D^{20} 1.4660; d_4^{20} 0.9399.

Found %: P 8.13, 8.26
$C_{20}H_{43}PO_2N_2$. Calculated %: P 8.26

Dipiperidide of 2-ethoxyvinylphosphonic acid $C_2H_5OCH=CHPO(NC_5H_{10})_2$. From 18 g of piperidine and 9.45 g of 2-ethoxyvinylphosphonic dichloride, 13.8 g of the dipiperidide of 2-ethoxyvinylphosphonic acid was obtained. After recrystallization from a mixture of petroleum ether and benzene it melted at 60-61°.

Found %: P 10.78, 10.82
$C_{14}H_{27}PO_2N_2$. Calculated %: P 10.83

Bisdibutylamide of 2-propoxyvinylphosphonic acid $n\text{-}C_3H_7OCH=CHPO[N(C_4H_9\text{-}n)_2]_2$. 2-Propoxyvinylphosphonic dichloride (10.2 g) was added to a solution of 28 g of dibutylamine in 150 ml of petroleum ether. The product isolated (13 g) had b.p. 172° (1 mm); n_D^{20} 1.4663; d_4^{20} 0.9301.

Found %: N 7.64, 7.48
$C_{21}H_{45}O_2PN_2$. Calculated %: N 7.21

Bisdimethylamide of 2-isopropoxyvinylphosphonic acid $i\text{-}C_3H_7-O-CH=CHPO[N(CH_3)_2]_2$. A solution of 9 g of dimethylamine in 10 ml of petroleum ether was added to a cooled mixture of 50 ml of petroleum ether and 50 ml of benzene, and then 10.15 g of 2-isopropoxyvinylphosphonic dichloride was added. The substance isolated (8 g, i.e., 73%) had b.p. 105.5° (2 mm): n_D^{20} 1.4742; d_4^{20} 1.0182.

Found %: N 12.55, 12.68
$C_{10}H_{21}PO_2N_2$. Calculated %: N 12.72

Bisdiethylamide of 2-isopropoxyvinylphosphonic acid $i\text{-}C_3H_7-O-CH=CHPO[N(C_2H_5)_2]_2$. Reaction between 14.5 g of diethylamine and 10.15 g of 2-isopropoxyvinylphosphonic dichloride yielded 7.5 g (55%) of a substance having b.p. 132° (2 mm): n_D^{20} 1.4709; d_4^{20} 0.9962.

Found %: N 10.07, 9.92
$C_{13}H_{29}O_2PN_2$. Calculated %: N 10.14

Bisdimethylamide of 2-butoxyvinylphosphonic acid $n\text{-}C_4H_9-O-CH=CHPO[N(CH_3)_2]_2$. Reaction between 10.85 g of 2-butoxyvinylphosphonic dichloride and 9 g of dimethylamine in a mixture of 50 ml of petroleum ether and 50 ml of benzene as solvent yielded 6 g (50%) of a substance having b.p. 116° (1 mm); n_D^{20} 1.4755; d_4^{20} 1.0090.

Found %: P 13.26, 13.20
$C_{10}H_{23}O_2N_2P$. Calculated %: P 13.24

Bisdiethylamide of 2-butoxyvinylphosphonic acid $n\text{-}C_4H_9-O-CH=CHPO[N(C_2H_5)_2]_2$. 2-Butoxyvinylphosphonic dichloride (10.85 g) was added gradually to 14.5 g of diethylamine. Three fractionations yielded 8 g (55%) of a substance having b.p. 130° (1 mm); n_D^{20} 1.4729; d_4^{20} 0.9745.

Found %: N 9.66, 9.29
$C_{14}H_{31}O_2N_2P$. Calculated %: N 9.65

Bisdibutylamide of 2-isopentyloxyvinylphosphonic acid $(CH_3)_2-CH-CH_2-CH_2-O-CH=CHPO[N(C_4H_9\text{-}n)_2]_2$. To 28 g of dibutylamine, 11.55 g of 2-isopentyloxyvinylphosphonic dichloride was added. The product isolated (10.3 g) had b.p. 192-193° (2 mm); n_D^{20} 1.4665; d_4^{20} 0.9249.

Found %: N 6.87, 6.91

$C_{23}H_{49}PO_2N_2$. Calculated %: N 6.73

Bisdimethylamide of 2-phenoxyvinylphosphonic acid $C_6H_5-O-CH=CHPO[N(CH_3)_2]_2$. To 9.5 g of dimethylamine, 11.85 g of 2-phenoxyvinylphosphonic dichloride was added. The yield of product was 6.5 g (50%), and it had b.p. 145° (2 mm); n_D^{20} 1.4658; d_4^{20} 1.1199.

Found %: N 10.90, 11.06

$C_{12}H_{19}O_2PN_2$. Calculated %: N 11.02

Bisdiethylamide of 2-phenoxyvinylphosphonic acid $C_6H_5-O-CH=CHPO[N(C_2H_5)_2]_2$. Reaction between 14.5 g of diethylamine and 11.85 g of 2-phenoxyvinylphosphonic dichloride yielded 9 g (58%) of a substance having b.p. 132° (1 mm); d_4^{20} 1.0402; n_D^{20} 1.5200.

Found %: N 8.94, 8.98

$C_{16}H_{27}O_2PN_2$. Calculated %: N 9.03

Bisdibutylamide of 2-phenoxyvinylphosphonic acid $C_6H_5OCH=CHPO[N(C_4H_9\text{-}n)_2]_2$. The bisdibutylamide of 2-phenoxyvinylphosphonic acid (12.5 g) was prepared from 27 g of dibutylamine and 11.85 g of 2-phenoxyvinylphosphonic dichloride. It had b.p. 213° (0.5 mm); n_D^{20} 1.5060; d_4^{20} 0.9886.

Found %: P 7.39, 7.24

$C_{24}H_{43}PO_2N_2$. Calculated %: P 7.34

Dipiperidide of 2-phenoxyvinylphosphonic acid $C_6H_5OCH=CHPO(NC_5H_{10})_2$. To 16.52 g of piperidine, 11.85 g of 2-phenoxyvinylphosphonic dichloride was added. Suitable treatment yielded 10 g of the dipiperidide of 2-phenoxyvinylphosphonic acid, b.p. 202° (1 mm); n_D^{20} 1.5528; d_4^{20} 1.1193.

Found %: P 9.29, 9.23

$C_{18}H_{27}PO_2N_2$. Calculated %: P 9.28

SUMMARY

The following compounds were synthesized by the reaction of secondary aliphatic amines with 2-alkoxy- and 2-phenoxy-vinylphosphonic dichlorides: the bisdimethylamides of 2-ethoxy-, 2-isopropoxy-, 2-butoxy, and 2-phenoxy-vinylphosphonic acids; the bisdiethylamides of 2-ethoxy-, 2-isopropoxy-, 2-butoxy-, and 2-phenoxy-vinylphosphonic acids; the bisdibutylamides of 2-ethoxy-, 2-propoxy-, 2-isopentyloxy-, and 2-phenoxy-vinylphosphonic acids; and the dipiperidides of 2-ethoxy-, 2-butoxy-, and 2-phenoxy-vinylphosphonic acids.

Received June 11, 1954

Institute of Heteroorganic Compounds of the
USSR Academy of Sciences

LITERATURE CITED

[1] A. Michaelis, Ann., 293, 193 (1896).

[2] A. Michaelis, Ann., 294, 1 (1896).

[3] A. Michaelis, Ann., 326, 129 (1903).

[4] A. Michaelis, Ann., 315, 43 (1901).

[5] M. I. Kabachnik, P. A. Rossiiskaya and N. N. Novikova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1947, No. 1, 47.

[6] P. A. Rossiiskaya and M. I. Kabachnik, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1947, No. 4, 389.

[7] M. I. Kabachnik and P. A. Rossiiskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1946, 515.

[8] A. Hamilton, U. S. Patent 2,365,466 (1944); U. S. Patent 2,382,309 (1945).

[9] K. N. Anisimov and A. N. Nesmeyanov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 4, 610. (T.p. 521).*

---

* T.p. = Consultants Bureau Translation pagination.

BLANK
PAGE

DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 9. DIESTERS OF 2-ALKOXY- AND 2-PHENOXY-VINYLPHOSPHONOTHIONIC ACIDS

K. N. Anisimov, N. E. Kolobova and A. N. Nesmeyanov

As shown in previous communications [1, 2], 2-alkoxy- and 2-phenoxy-vinylphosphonic dichlorides react fairly readily with alcohols and with secondary amines, forming diesters and bisdialkylamides, respectively, of 2-alkoxy- and 2-phenoxy-vinylphosphonic acids. 2-Alkoxy- and 2-phenoxy-vinylphosphonothionic dichlorides are considerably more inert, and they do not react with alcohols or with amines under the conditions that we have described previously for the synthesis of esters and bisdialkylamides of unsaturated phosphonic acids.

We have now prepared diesters of 2-alkoxy- and 2-phenoxy-vinylphosphonothionic acids by the action of the corresponding acid chlorides on a sodium alkoxide in an excess of the alcohol. The compounds listed in the table were synthesized under these conditions. The 2-alkoxy- and 2-phenoxy-vinylphosphonothionic dichlorides were prepared by a method developed by us [3]. All of the esters that we have prepared are colorless liquids, which are insoluble in water, but soluble in ether, benzene, acetone, and other organic solvents.

TABLE

Formula	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}
$C_2H_5-O-CH=CHPS(OCH_3)_2$	86 (1)	1.4852	1.1373
$i\text{-}C_3H_7-O-CH=CHPS(OCH_3)_2$	95 (1)	1.4780	1.1035
$n\text{-}C_4H_9-O-CH=CHPS(OCH_3)_2$	107 (1)	1.4790	1.1018
$C_6H_5-O-CH=CHPS(OCH_3)_2$	151 (2)	1.5331	1.1945
$C_2H_5-O-CH=CHPS(OC_2H_5)_2$	107 (3)	1.4879	1.0970
$i\text{-}C_3H_7-O-CH=CHPS(OC_2H_5)_2$	105 (1)	1.4741	1.0510
$n\text{-}C_4H_9-O-CH=CHPS(OC_2H_5)_2$	117 (1)	1.4705	1.0687
$C_6H_5-O-CH=CHPS(OC_2H_5)_2$	159 (2)	1.5375	1.1263

EXPERIMENTAL

Dimethyl 2-ethoxyvinylphosphonothionate $C_2H_5-O-CH=CHPS(OCH_3)_2$. Absolute methanol (50 ml) and sodium (2.3 g) were introduced into a three-necked flask fitted with stirrer, reflux condenser, and dropping funnel. The resulting solution of sodium methoxide was cooled, and was then stirred while 10.2 g of 2-ethoxyvinylphosphonothionic dichloride was added gradually. When the whole of this had been added, the mixture was stirred for three hours and was then set aside overnight. On the next day 100 ml of absolute ether was added to the mixture. The mixture was warmed in a water bath (55-60°), where it was stirred for two hours. The ether layer was poured off and the precipitate was washed twice with ether. The ether solution was dried over Na_2SO_4. Vacuum fractionation yielded 6.5 g (60%) of a substance having b.p. 86° (1 mm); n_D^{20} 1.4852; d_4^{20} 1.1373.

Found %: P 15.81, 15.72

$C_6H_{13}O_3PS$. Calculated %: P 15.81

Dimethyl 2-isopropoxyvinylphosphonothionate $i\text{-}C_3H_7-O-CH=CHPS(OCH_3)_2$. 2-Isopropoxyvinylphosphonothionic dichloride (10.95 g) was diluted with an equal volume of absolute methanol and then added with cooling and stirring to a solution of sodium methoxide prepared from 50 ml of absolute methanol and 2.3 g of sodium. The product isolated (9.7 g, i.e., 86%) had b.p. 101° (2 mm); n_D^{20} 1.4780; d_4^{20} 1.1035.

Found %: P 14.73, 14.69

$C_7H_{15}O_3PS$. Calculated %: P 14.76

Dimethyl 2-butoxyvinylphosphonothionate $n\text{-}C_4H_9{-}O{-}CH{=}CHPS(OCH_3)_2$. A solution of 11.65 g of 2-butoxyvinylphosphonothionic dichloride in 12 ml of absolute methanol was added to sodium methoxide prepared from 2.3 g of sodium and 56 ml of absolute methanol. The pure product isolated (9.1 g, i.e., 70%) had b.p. 107° (1 mm); n_D^{20} 1.4790; d_4^{20} 1.1018.

Found %: P 13.88, 13.81
$C_8H_{17}O_3PS$. Calculated %: P 13.83

Dimethyl 2-phenoxyvinylphosphonothionate $C_6H_5{-}O{-}CH{-}CHPS(OCH_3)_2$. A solution of 12.65 g of 2-phenoxyvinylphosphonothionic dichloride in 20 ml of absolute methanol was added to sodium methoxide prepared from 50 ml of absolute methanol and 2.3 g of sodium. Vacuum fractionation of the crude product (9 g) yielded 6.6 g (50%) of a substance having b.p. 151° (2 mm); n_D^{20} 1.5531; d_4^{20} 1.1945.

Found %: P 12.59, 12.60
$C_{10}H_{13}O_3PS$. Calculated %: P 12.70

Diethyl 2-ethoxyvinylphosphonothionate $C_2H_5{-}O{-}CH{=}CHPS(OC_2H_5)_2$. 2-Ethoxyvinylphosphonothionic dichloride (12.2 g) was added to sodium ethoxide prepared from 2.3 g of sodium and 60 ml of absolute ethanol. The product isolated (6.2 g, i.e., 50%) had b.p. 100° (1 mm); n_D^{20} 1.4879; d_4^{20} 1.0970.

Found %: P 13.87; 13.64
$C_8H_{17}O_3PS$. Calculated %: P 13.83

Diethyl 2-isopropoxyvinylphosphonothionate $i\text{-}C_3H_7{-}O{-}CH{=}CHPS(OC_2H_5)_2$. 2-Isopropoxyvinylphosphonothionic dichloride (10.95 g) was added to sodium ethoxide prepared from 50 ml of absolute ethanol and 2.3 g of sodium. The product isolated (8 g, i.e., 63%) had b.p. 105° (1 mm); n_D^{20} 1.4741; d_4^{20} 1.0510.

Found %: P 13.07, 12.89
$C_9H_{19}O_3PS$. Calculated %: P 13.02

Diethyl 2-butoxyvinylphosophonothionate $n\text{-}C_4H_9{-}O{-}CH{=}CHPS(OC_2H_5)_2$. 2-Butoxyvinylphosphonothionic dichloride (11.65 g) was added to sodium ethoxide prepared from 2.3 g of sodium and 80 ml of absolute ethanol. The product isolated (8 g, i.e., 60%) had b.p. 107° (1 mm); n_D^{20} 1.4705; d_4^{20} 1.0687.

Found %: P 12.27, 12.29
$C_{10}H_{21}O_3PS$. Calculated %: P 12.30

Diethyl 2-phenoxyvinylphosphonothionate $C_6H_5{-}O{-}CH{=}CHPS(OC_2H_5)_2$. 2-Phenoxyvinylphosphonothionic dichloride (12.65 g) was added to sodium ethoxide prepared from 2.3 g of sodium and 50 ml of absolute ethanol. Fractionation of the crude product (12 g) yielded 7.8 g (75%) of a substance having b.p. 139° (2 mm); n_D^{20} 1.5375, d_4^{20} 1.1263.

Found %: P 11.43, 11.44
$C_{12}H_{17}O_3PS$. Calculated %: P 11.39

SUMMARY

By the action of 2-ethoxy-, 2-isopropoxy-, 2-butoxy-, and 2-phenoxy-vinylphosphonothionic dichlorides on sodium methoxide and on sodium ethoxide in the form of solutions in the corresponding alcohols, the dimethyl and diethyl esters of 2-ethoxy-, 2-isopropoxy-, 2-butoxy-, and 2-phenoxy-vinylphosphonothionic acids were prepared.

Received June 11, 1954

Institute of Heteroorganic Compounds of
the USSR Academy of Sciences

LITERATURE CITED

[1] K. N. Anisimov, N. E. Kolobova and A. N. Nesmeyanov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, No. 2, 240. (T.p. 213).*

[2] K. N. Anisimov, N. E. Kolobova and A. N. Nesmeyanov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, No. 4, 665. (T.p. 591).*

[3] K. N. Anisimov, N. E. Kolobova and A. N. Nesmeyanov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 5, 797. (T.p. 685).*

---

* T.p. = Consultants Bureau Translation pagination.

SOME ESTERS OF PHOSPHORODITHIOIC ACID AS INSECTICIDES

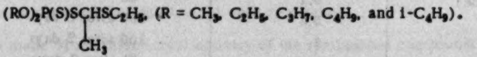
B. A. Arbuzov, K. V. Nikonorov, and G. M. Vinokurova

As is well known, derivatives of thiophosphoric acids are used extensively in agriculture as insecticides; they are found to be very effective against many kinds of harmful insects. Among the many compounds of this sort there are the well known trimethyl phosphorothioate O,O-diethyl O-p-nitrophenyl phosphorothioate (parathion, thiophos), and the O-ester of 4-methylumbelliferone with O,O-diethyl phosphorothioate (potasan) [1]. O,O-Diethyl O-2-(ethylthio)ethyl phosphorothioate (systox) [2] is of great interest. This compound, while having a comparatively feeble contact action, is a good insecticide on account of internal (systemic) action. Systox can be used successfully as a nematocide [3].

Interest has grown recently in the mixed esters of phosphorodithioic acid. These substances, while having fairly high insecticidal activity, are safer for warm-blooded animals, including man, than the esters of phosphoric and phosphorothioic acids [4]. A compound of this type that has found practical application in agriculture is S-[1,2-bis(ethoxycarbonyl)ethyl] O,O-dimethyl phosphorodithioate (malathion) [5].

In 1952 and 1953 some phosphorodithioic esters were described of general formula $(RO)_2P(S)SCH(R')XR''$ (X= =O or S and R, R', and R'' are aliphatic or aromatic radicals). All of these were found to be powerful insecticides [6].

In this paper we describe the synthesis of compounds of the type



$$(RO)_2P(S)S\underset{\displaystyle CH_3}{\underset{|}{C}}HSC_2H_5, \ (R = CH_3, C_2H_5, C_3H_7, C_4H_9, \text{ and } i\text{-}C_4H_9).$$

It was found that these substances can be readily prepared by the condensation of the corresponding O,O-dialkyl S-hydrogen phosphorodithioates with acetaldehyde and ethanethiol in accordance with the equation:

$$(RO)_2P(S)SH + CH_3CHO + HSC_2H_5 = (RO)_2P(S)SCH(CH_3)SC_2H_5 + H_2O.$$

The resulting compounds were colorless liquids of unpleasant odor. The lower esters (up to propyl, inclusive) could be vacuum-distilled (at 2-3 mm) with partial decomposition; the butyl esters decomposed completely during distillation. The principal constants of the compounds obtained are given in Table 1.

The insecticidal activity of the compounds was tested on the corn weevil. The results of the tests are given in Table 2.

As can be seen from Table 2, the first two compounds have higher insecticidal activity than the succeeding compounds. On the whole, however, these esters are fairly weak insecticides. The tests for insecticidal activity were carried out in the toxicological laboratory of the Kazan Affiliated Institute of the Academy of Sciences of the USSR by M. A. Kudrina.

EXPERIMENTAL

Action of Acetaldehyde and Ethanethiol on O,O-Dimethyl Phosphorodithioate

A mixture of 20 g of O,O-dimethyl phosphorodithioate and 8.1 g of ethanethiol was placed in a three-necked flask fitted with reflux condenser, thermometer, stirrer, and dropping funnel. The mixture was cooled to –10° and stirred continuously while 5.5 g of acetaldehyde was added dropwise at such a rate that the temperature did not rise above 0°. When the addition was complete, stirring was continued for a further two hours at room temperature. After the whole of the aldehyde had been added the formation of some water (about 2 ml) was observed This water was removed, and the organic layer was vacuum-distilled. Pure $(CH_3O)_2P(S)SCH(CH_3)SC_2H_5$ has b.p. 82-83° (4 mm), n_D^{20} 1.5320; and d_4^{20} 41 1788. The yield was 28.70%.

Found %: P 12.95; 12.60

$C_6H_{15}S_3O_2P$. Calculated %: P 12.6

TABLE 1

Formula	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	Yield (%)
$(CH_3O)_2\underset{\underset{S}{\parallel}}{P}SCH(CH_3)SC_2H_5$	82-83 (4)	1.1788	1.5320	28.7
$(C_2H_5O)\underset{\underset{S}{\parallel}}{P}SCH(CH_3)SC_2H_5$	118-119 (3)	1.1347	1.5240	39.6
Ditto (crude)	–	1.1351	1.5230	70.9
$(C_3H_7O)_2\underset{\underset{S}{\parallel}}{P}SCH(CH_3)SC_2H_5$	122-128 (4)	1.0929	1.5130	49.3
$(C_4H_9O_2)\underset{\underset{S}{\parallel}}{P}SCH(CH_3)SC_2H_5$ (crude)	–	1.0600	1.5085	73.5
$(i\text{-}C_4H_9O)_2\underset{\underset{S}{\parallel}}{P}S\underset{\underset{CH_3}{\vert}}{C}HSC_2H_5$ (crude)	–	1.0522	1.5060	67.6

TABLE 2

Formula	Concentration (%)	Proportion of corn weevils killed (%)
$(CH_3O)_2\underset{\underset{S}{\parallel}}{P}SCH(CH_3)SC_2H_5$	0.1	25 after 7days
	0.5	65 ditto
	1	85 "
$(C_2H_5)_2\underset{\underset{S}{\parallel}}{P}SCH(CH_3)SC_2H_5$ (crude)	0.1	32 "
	0.5	100 after 3 days
	1	100 after 2 days
$(C_3H_7O)_2\underset{\underset{S}{\parallel}}{P}SCH(CH_3)SC_2H_5$	0.1	12 after 7 days
	0.5	16 ditto
	1	18 "
$(C_4H_9O)_2\underset{\underset{S}{\parallel}}{P}SCH(CH_3)SC_2H_5$ (crude)	0.1	12 "
	0.5	20 "
	1	24 "
$(i\text{-}C_4H_9O)_2\underset{\underset{S}{\parallel}}{P}SCH(CH_3)SC_2H_5$ (crude)	0.1	66 "
	0.5	10 "
	1	12 "

Action of Acetaldehyde and Ethanethiol on O, O-Diethyl Phosphorodithioate

Experiment 1. Acetaldehyde (3.5 g) was added to a mixture of 15 g of O, O-diethyl phosphorodithioate and 5.01 g of ethanethiol. The water that separated was taken up with phosphoric oxide. The reactionnmixture was stirred at room temperature for 30 minutes and then vacuum-distilled from an Arbuzov flask. The product isolated had b.p. 118-119° (3 mm); n_D^{20} 1.5240; d_4^{20} 1.1347. The yield was 39.6%

Found %: 12.18: 11.78; S 35.24

$C_6H_{15}O_2S_3P$. Calculated %: P 11.31; S 35.04

Experiment 2. Reaction was between 20 g of O, O-diethyl phosphorodithioate, 4.7 g of acetaldehyde, and 6.6 g of ethanethiol. The reaction product was washed with 10% sodium carbonate solution and then water. It was then dried with calcium chloride and analyzed. The product had n_D^{20} 1.5230 and d_4^{20} 1.1351.

Found %: P 11.26, 11.19; S 35.22; 35.01

$C_6H_{15}O_2S_3P$. Calculated %: P 11.31; S 35.06

Action of Acetaldehyde and Ethanethiol on O, O-Dipropyl Phosphorodithioate

The reactants were $(C_3H_7O)_2PSSH$ (20 g), C_2H_5SH (5.9 g), and CH_3CHO (4.1 g). The reaction mixture was stirred at room temperature for four hours. Fractionation yielded two fractions: the first was unchanged dipropyl phosphorodithioate, and the second was the required ester, b.p. 122-128 (4 mm); n_D^{20} 1.5130; d_4^{20} 1.0929. The yield was 49%.

Found %: P 10.99, 10.92

$C_{10}H_{23}O_2PS_3$. Calculated %: P 10.26

Action of Acetaldehyde and Ethanethiol on O,O-Dibutyl Phosphorodithioate

The procedure was as in the preceding experiment, the reactants being O,O-dibutyl phosphorodithioate (10 g), ethanethiol (2.5 g), and acetaldehyde (1.8 g). The reaction product was washed with 10% aqueous sodium carbonate solution and with water, then dried with calcium chloride and analyzed. The product had n_D^{20} 1.5085; d_4^{20} 1.060. The yield was 73.5%.

Found %: P 9.46; 9.35

$C_{12}H_{27}S_3PO_2$. Calculated %: P 9.4

An attempt to distill the substance under reduced pressure (1-2 mm) was not successful, for at a bath temperature of about 150° decomposition set in.

Action of Acetaldehyde and Ethanethiol on O,O-Diisobutyl Phosphorodithioate

The reactants were O,O-diisobutyl phosphorodithioate (10 g), ethanethiol (2.5 g), and acetaldehyde (1.8 g) (cf. previous experiment). The reaction product decomposed when vacuum-distilled. Its purification consisted in a wash with water and drying over calcium chloride. The yield was 67.6%, and the compound had n_D^{20} 1.5060; d_4^{20} 1.0522.

Found %: P 9.50; 9.22

$C_{12}H_{27}S_3O_2P$. Calculated %: P 9.4

SUMMARY

1. By the condensation of O,O-dialkyl phosphorodithioates with acetaldehyde and ethanethiol, five previously undescribed mixed esters of phosphorodithioic acid were synthesized.

2. A study was made of the insecticidal activity of the synthesized compounds with respect to the corn weevil.

Received June 1, 1954

A. E. Arbuzov Chemical Institute of the
Kazan Affiliated Institute of the USSR
Academy of Sciences

LITERATURE CITED

[1] G. Schrader, Die Entwicklung neuer Insektizide auf Grundlage organischer Fluor- und Phosphor-Verbindungen, Weinheim, 1951.

[2] R. Jefferson, J. Econ. Entomol. 44, 1021 (1951).

[3] P. Miller, Agric. Chemicals, 6, (6), 63, 103 (1951).

[4] Agric. Chemicals 6. I. 53, 83 (1951).

[5] I. Schread, Chem. Abs., 46, 217 (1952); J. Econ. Entomol., 45, 761 (1952).

[6] O. Hoon and P. H. Moss, Chem. Abs., 8322 (1952); Chem. Z., 14, 2182 (1953).

BLANK
PAGE

ACTION OF HALOGENS ON ESTERS OF ANTIMONOUS ACID

B. A. Arbuzov and O. D. Samoilova

Addition reactions are characteristic of both phosphorous and arsenious esters, but whereas phosphorous esters are converted by halogens into quinquevalent phosphorous compounds by Arbuzov rearrangement [1], arsenious esters form only addition compounds with halogens [2].

Antimonous esters have a pair of unshared electrons on the antimony atom and therefore should be capable of undergoing addition reactions to some extent.

The results of reactions that we have carried out show that triethyl and tributyl antimonites readily form addition products with chlorine and bromine.

Trialkoxystibine dihalides decompose when heated. Trialkoxystibine dichlorides decompose with the formation of the alkyl chloride, an ether, and antimony trichloride. Trialkoxystibine dibromides decompose in a more complicated fashion with formation of an ether, the alkyl bromide, an alcohol, an ester of a carboxylic acid, and antimony tribromide. The decomposition of trialkoxystibine dibromides in such a complex way is probably to be explained by the following properties of antimonous esters. We have shown previously that the Tishchenko ester condensation of aldehydes can be effected not only with aluminum and zinc alkoxides, but also, to a greater or less extent, with Zr, Ti, Sn^{IV}; Sb^{III}, and Sb^{V} alkoxides; the alkoxides of these same metals are able to reduce aldehydes to alcohols [3].

In 1951 Nesmeyanov and coworkers found [4] that the action of halogens on tetraalkyl orthotitanates was accompanied by the elimination of an alcohol and an ester and the formation of dialkyldihalotitanium. The alcohol and ester were formed as a result of a peculiar disproportionation of the two alkoxy groups with the simultaneous formation of equimolecular amounts of alcohol and aldehyde. The latter underwent Tishchenko ester condensation in presence of the tetraalkyl orthotitanate.

In view of the tendency of the esters of antimony acids to promote the ester condensation of aldehydes and to reduce aldehydes to alcohols, we considered that it might be assumed that the complex decomposition of trialkoxystibine dibromides proceeds partially by the scheme proposed by Nesmeyanov for tetraalkyl orthotitanates:

$$\begin{aligned} SbBr_2(OCH_2R)_3 &\rightarrow SbBr_2(OCH_2R) + 2RCH_2O\cdot; \\ 2RCH_2O\cdot &\rightarrow RCH_2OH + RCHO; \\ RCHO &\rightarrow RCOOCH_2R; \\ RCHO &\rightarrow RCH_2OH; \\ SbBr_2(OCH_2R) &\rightarrow SbOBr + RCH_2Br. \end{aligned}$$

The reducing properties of trialkoxystibine dibromides and their ability to effect the ester condensation of aldehydes was confirmed by us in experiments with benzaldehyde and isobutyraldehyde. In these reactions the corresponding alcohols and esters of the corresponding acids were isolated. When an alcoholic solution of benzaldehyde was boiled for a long time with triethoxystibine dichloride, the subsequent fractional distillation yielded only benzaldehyde.

EXPERIMENTAL

Action of Chlorine on Triethyl Antimonite.

A flask containing 30 g of triethyl antimonite dissolved in chloroform (55 g) was cooled with snow, and dry chlorine was passed in until the weight increased by 7.5 g. In view of the instability of antimonous esters to hydrolysis, all reactions were carried out with exclusion of atmospheric moisture. When reaction was complete, chloroform was distilled off under somewhat reduced pressure from a water bath at 45-50°. After being recrystallized from ether, triethoxystibine dichloride melted at 50-53°.

Found %: Sb 36.67; 36.51; Cl 21.92; 22.08
$C_6H_{15}O_3Cl_2Sb$. Calculated %: Sb 37.18; Cl 21.68

Triethoxystibine dichloride (30 g) was subjected to thermal decomposition in a flask carrying a Vigreux column and connected to traps.

When the oil-bath temperature reached 100° the crystalline substance melted, but no low-boiling fractions came over. At 145-150° vigorous decomposition set in. A low-boiling liquid collected in the trap; we did not succeed in determining the physical constants of this substance (it burned with a green flame). The yield of liquid was 2.1 g, or 7% of the amount taken. It appeared to be ethyl chloride, the reported boiling point of which is 12.5° [5]. Another liquid fraction, amounting to 6.8 g (22.8%) was collected. It had a boiling point of 34-36°, corresponding to diethyl ether.

After the thermal decomposition 18.8 g (60.2%) of a solid porous mass remained, and when this was distilled at 116-118° (10 mm), 2.6 g (60.2%) of a white crystalline substance was obtained. It had a melting point of 70-72°, corresponding to antimony trichloride, for which the literature [6] gives b.p. 223°, m.p. 73°.

Action of Bromine on Triethyl Antimonite. A chloroform solution of 30 g of triethyl antimonite was placed in a flask fitted with reflux condenser, and with snow cooling 18.6 g of bromine was carefully added. Each drop of bromine was immediately decolorized, but when the final addition was made decolorization was slower. Chloroform was then removed under somewhat reduced pressure from a water bath at 45-50°. The thick yellowish residue crystallized when dried in a vacuum desiccator. After being washed with ether and dried, the crystalline substance melted at 64-67°.

Found %: Sb 29.20; 29.70

$C_6H_{15}O_3Br_2Sb$. Calculated %: Sb 29.21

This bromine-addition product (45 g) was subjected to thermal decomposition.

When the oil-bath temperature reached 110° the crystalline substance melted, but there was not a drop of low-boiling liquid on the walls of the flask. At 130-135° there was vigorous decomposition with frothing. The liquid fraction collected (19 g) boiled over the range 60-158°. A solid porous mass (21.5 g) remained in the flask. Fractionation of the liquid products yielded:

Fraction I,	b.p.	37 - 40°;	8.5 g
Fraction II,	b.p.	45 - 75°;	a few drops
Fraction III,	b.p.	77 - 79°;	4.1 g
Fraction IV,	b.p.	52 - 65° (14 mm);	2.9 g

Fraction I (8.5 g, b.p. 37-40°) was treated with a few drops of sulfuric acid in a flask fitted with a reflux condenser. From the resulting product 5.1 g of ethyl bromide, b.p. 38-39°, was isolated (the theoretically required amount is 11.7 g); about 3 g of diethyl ether was isolated.

Fraction II, b.p. 77 - 79°, had d_4^{20} 0.8005. The melting point of the p-nitrobenzoic ester of this substance was 56 - 57°. The amount isolated was 4.1 g.

These results indicate that Fraction II was ethanol. The literature [7] gives b.p. 78.3°, d_4^{20} 0.7898; p-nitrobenzoic ester, m.p. 57°.

Fraction IV was repeatedly distilled and yielded 2.2 g of a substance having b.p. 53 - 65° (14 mm); d_4^{20} 1.5059; n_d^{20} 1.4592; found MR 30.33; calculated MR 30.16. The substance irritated the mucous membrane of the eye. This fraction was ethyl bromoacetate. The literature [8] gives b.p. 168.7°; n_d^{13} 1.4542; d_4^{13} 1.5141 [8].

Action of Chlorine on Tributyl Antimonite. Dry chlorine was passed into a water-cooled flask containing 25 g of tributyl antimonite until the weight had increased by 5.2 g. A thick, yellowish liquid, d_4^{20} 1.4073, was formed.

Found %: Sb 30.33; 29.91

$C_{12}H_{27}O_3Cl_2Sb$. Calculated %: Sb 29.57

Tributoxystibine dichloride (27 g) was subjected to thermal decomposition in a flask fitted with a fractionating column. At an oil-bath temperature of 130-135°, vigorous decomposition set in. The following fractions were collected:

Fraction I,	b.p.	75 - 79°;	3.7 g
Fraction II,	b.p.	139 - 142°;	7.1 g

After the thermal decomposition, 14.2 g (52.6%) of a black, porous mass remained, and from this 2.12 g of a white, crystalline substance was isolated. It had b.p. 114-115° (8 mm), and m.p. 70-72°. It was antimony trichloride.

After being redistilled, Fraction I had b.p. 77 - 78° and d_4^{20} 0.8862; it was butyl chloride, for which the literature [9] gives b.p. 79° and d_0^{14} 0.8972 [9].

After being redistilled, Fraction II had b.p. 46 - 47° (14 mm); d_4^{20} 0.7814; n_d^{20} 1.4054; it was dibutyl ether, for which the literature [10] gives b.p. 140.9° and d_4^0 0.7841 [10].

Action of Bromine on Tributyl Antimonite. Tributyl antimonite (25 g) was treated cautiously under cooling with bromine (11.7 g). Each drop of bromine was immediately decolorized. The product was a thick, reddish liquid, which did not crystallize out when cooled. It had d_4^{20} 1.7052.

Found %: Sb 24.80; 24.51
$C_{12}H_{27}O_3Br_2Sb$. Calculated %: Sb 24.88

Tributoxystibine dibromide (36 g) was subjected to thermal decomposition. Vigorous decomposition began at an oil-bath temperature of 125 - 130°. Altogether, 18 g of a liquid fraction came over at 74 - 153°. The residue was 17.9 g (46.8%) of a black solid porous mass. This mass yielded 1.2 g of a white, crystalline substance melting at 95 - 97° and boiling at 165 - 168° (4 mm). It was antimony tribromide, for which the literature [6] gives m.p. 94°, b.p. 280°. The liquid fraction was fractionated through a Vigreux column and yielded:

Fraction I,	b.p. 74 - 82°;	1.1 g
Fraction II,	b.p. 85 - 104°;	2.2 g
Fraction III,	b.p. 113 - 117°;	10.2 g
Fraction IV,	b.p. 42 - 45° (12 mm);	2.1 g
Fraction V,	b.p. 56 - 62° (12 mm);	1.6 g

The fractions were redistilled. Fraction I (0.8 g, i.e. 2.2%) then boiled at 75-78° and had d_4^{20} 0.8296; it gave a reddish precipitate with 2,4-dinitrophenylhydrazine. It was butyraldehyde, for which the literature [11] gives b.p. 75°, d_4^{20} 0.8170; n_D^{20} 1.38433. Fraction II (1.6 g, i.e. 4.4%; b.p. 101-104°, d_4^{20} 1.2667, and n_D^{20} 1.4314) was butyl bromide, for which the literature [9] gives b.p. 99.88° and d_0^{20} 1.299. Fraction III (10.4 g, i.e. 28.9%; b.p. 114-117°, d_4^{20} 0.8151, and n_D^{20} 1.4012) was butyl alcohol, for which the literature [12] gives b.p. 116.7°, d_4^{20} 0.8099, and n_D^{20} 1.39909. Fraction IV (1.6 g, i.e. 4.4%; b.p. 43-44°/ 12mm, d_4^{20} 0.7809; n_D^{20} 1.4042) was dibutyl ether, for which the literature [10] gives b.p. 140.9° and d_4^0 0.7841. Fraction V (0.9 g, i.e. 2.5%; b.p. 58-61°/ 12 mm, d_4^{20} 0.8784, and n_D^{20} 1.4086) was butyl butyrate: found MR 40.32; calculated MR 40.97. The literature [9] gives b.p. 164.8°, d_{20}^{20} 0.8717 [9].

Action of Triethoxystibine Dibromide on Benzaldehyde. An alcoholic solution of 25 g of benzaldehyde (b.p. 67-68° at 11 mm) was boiled under reflux with 3 g of triethoxystibine dibromide for 25 hours. After two hours a white precipitate appeared in the reaction mixture, and the amount of this increased as the reaction proceeded. When the operation was complete the white precipitate was centrifuged off; it weighed 2.6 g. The alcoholic solution of reaction products was fractionally distilled. In a second distillation the following fractions were collected:

Fraction I,	b.p. 66 - 67° (11 mm);	14.3 g
Fraction II,	b.p. 86 - 87° (11 mm);	2.8 g
Fraction III,	b.p. 90 - 91° (11 mm);	2.4 g

The boiling point of Fraction I indicates that it was unchanged benzaldehyde (57.2% of the amount taken). Fraction II (2.8 g, i.e. 11.2%; b.p. 86-87°/11mm, d_4^{20} 1.0428; n_D^{20} 1.5342) was benzyl alcohol, for which the literature [13] gives b.p. 204.5 - 205.5°, n_D^{20} 1.53955; d_4^{20} 1.0429 [13].

Fraction III (2.4 g, i.e. 9%; b.p. 90 - 91°/ 11 mm, d_4^{20} 1.0497, and n_D^{20} 1.5049) was ethyl benzoate, for which the literature [14] gives b.p. 211.2°, d_4^{15} 1.0509, and n_D^{15} 1.5079.

After the first fractionation there was a black crystalline residue. Recrystallization from ligroin yielded white crystals, which yellowed somewhat when exposed to air. Its melting point, which was 63 - 64° after several recrystallizations, indicates that it was phenyl m-bromobenzoate, for which the literature [15] gives m.p. 65°. The yield of crude product was 1.2 g.

Action of Tributoxystibine Dibromide on Isobutyraldehyde. A mixture of 30 g of isobutyraldehyde and 5 g of tributoxystibine dibromide was prepared in a sealed tube. Reaction began at room temperature, so that the reaction mixture became appreciably warm, the bromine color disappeared, and a white precipitate appeared. The sealed tube was heated for six hours at 90 - 100°. The precipitate was centrifuged off, and the supernatant liquid was fractionally distilled. Redistillation yielded the following fractions:

Fraction I, b.p. 64 - 66°; 20.2 g
Fraction II, b.p. 106 - 112°; 1.8 g
Fraction III, b.p. 114 - 148°; 3.5 g
Residue 5 g

The boiling point of Fraction I indicated that it was unchanged isobutyraldehyde. Fraction II (b.p. 106 - 112°, d_4^{20} 0.8034) was isobutyl alcohol, for which the literature [16] gives b.p. 108.39° and d_0^{18} 0.8003. Fraction III (b.p. 144 - 148°, d_4^{20} 0.8728) was isobutyl isobutyrate, for which the literature [17] gives b.p. 146.6° and d_4^{20} 0.87495.

Action of Tributoxystibine Dichloride on Benzaldehyde. An alcoholic solution of 30 g of benzaldehyde was refluxed for 25 hours with 3 g of tributoxystibine dichloride. During this time no changes were observed in the reaction mixture. Fractionation of the mixture gave the original substances.

SUMMARY

1. Chlorine and bromine readily form addition products with antimonous esters.

2. The course of the thermal decomposition of trialkoxystibine dibromides is more complex than that of trialkoxystibine dichlorides. Trialkoxystibine dichlorides decompose with formation of an alkyl chloride, an ether, and antimony trichloride, while trialkoxystibine dibromides yield an alkyl bromide, an ether, an alcohol, and a carboxylic ester.

3. Trialkoxystibine dibromides are able to promote the Tishchenko ester condensation of aldehydes, and they are also able to reduce aldehydes.

LITERATURE CITED

[1] N. A. Menshutkin, Ann 139, 343 (1886); H. Wichelhaus, Ann. 6, 257 (1868).

[2] I. M. Crafts, Bull. 2, 14, 101 (1870).

[3] H. Meerwein and others, J. prak. Chem. 147, 211 (1936).

[4] A. N. Nesmeyanov, R. Kh. Freidlina, and O. V. Nogina, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1951, No. 5, 518.

[5] A. E Arbuzov, Structure of Phosphorous Acid and its Derivatives, St. Petersburg, 1905.

[6] D. I. Mendeleev, Fundamentals of Chemistry, Vol. 2, 1928, p. 369.

[7] I. W. Winkler, Ber., 38, 3615 (1905); D. I. Mendeleev, Ann. Physik.138, 103 (1869); I. Wiebrand, F. Beilstein, Ann. 128, 268 (1863).

[8] W. H. Perkin, J. Chem. Soc. 65, 427 (1894).

[9] E. Linnemann, U. Zotta, Ann. 161, 197 (1872).

[10] P. Dobriner, Ann, 243, 8 (1888).

[11] A. E. Chichibabin, Ber. 37, 188 (1904); I. W. Brühl, Ann. 203, 18 (1880).

[12] R. Schiff, Ann. 220, 101 (1883); I. W. Brühl, Ann. 203, 16 (1880).

[13] R. Schiff, Ber. 19, 561 (1886).

[14] A. Liben, A. Possi, Ann. 158, 168 (1871).

[15] H. F. Mügge, Jahrber, u. d. Fortschr. 676 (1879); 357 (1880).

[16] E. Linnemann, Ann. 160, 238 (1871).

[17] E. Elsässer, Ann. 218, 335 (1883).

Received July 9, 1954

A. M. Butlerov Research Institute of the
V. I. Ulyanov-Lenin Kazan State University

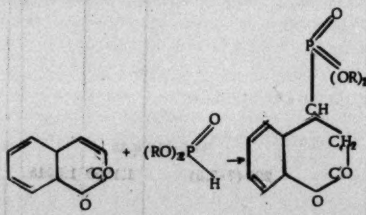
SYNTHESIS OF PHOSPHONIC ESTERS CONTAINING HETEROCYCLIC RADICALS

COMMUNICATION 5. PHOSPHONIC ESTERS CONTAINING A HYDROCOUMARIN RADICAL

B. A. Arbuzov and V. M. Zoroastrova

This paper is one of a series on the synthesis and properties of phosphonic esters containing heterocyclic groups [1, 2, 3, 4].

We have effected the syntheses of phosphonic esters in which phosphorus is attached to a heterocycle by the method discovered by Arbuzov and Pudovik [5], who carried out the addition of diethyl hydrogen phosphite to chloromethoxypentenes, and further developed in investigations by Pudovik. In presence of a sodium alkoxide, an alkyl diphosphite will add to an α, β-unsaturated ketone with formation of esters of γ-keto phosphonic acids. It would be expected that coumarin and its homologs would undergo a similar addition reaction with formation of esters of "hydrocoumarin-4-ylphosphonic acid":



The experiments that we have now carried out show that dialkyl phosphites add to coumarin and to 4-methylcoumarin (in presence of sodium alkoxides as catalysts) with formation of hydrocoumarinylphosphonic esters. Analogy with the addition products formed by dialkyl phosphites with α, β-unsaturated ketones indicated the position taken up by the phosphonic grouping in the hydrocoumarin nucleus. Addition of the dialkyl phosphite at the carbonyl group or with cleavage of the lactone ring is much less probable.

To check these possibilities we attempted to bring about the addition of diethyl phosphite to hydrocoumarin, and negative results were obtained, the original substances being recovered unchanged even when severe conditions were used. On the basis of these results it may be considered that addition of dialkyl phosphites occurs at the $-C=C-$bond.

Hydrolysis of the hydrocoumarin-4-yl- and 4-methylhydrocoumarin-4-yl-phosphonic esters with hydrochloric acid yielded, respectively, hydrocoumarin-4-ylphosphonic acid, m.p. 218-220° and 4-methylhydrocoumarin-4-ylphosphonic acid, m.p. 192-193°. The constants and yields of the compounds obtained are given in the table.

Unusual ease of reaction with diethyl phosphite was shown by 3-acetylcoumarin. Thus, when 3-acetylcoumarin and diethyl phosphite were heated with a little sodium ethoxide at 120°, reaction was complete in two hours. The product was a crystalline substance melting at 146-149° (from methanol) and corresponding in analysis to the product of the addition of one molecule of diethyl phosphite to one molecule of acetylcoumarin.

We did not succeed in obtaining a phenylhydrazone from the addition product formed by diethyl phosphite with 3-acetylcoumarin, although acetylcoumarin itself reacts readily with phenylhydrazine to form a crystalline phenylhydrazone melting at 182-183°. The possibility that diethyl phosphite added at the carbonyl group of the acetyl radical cannot be excluded, and the formula given for this compound in the table must be regarded as tentative.

It is notable that the determined molecular refraction values differ greatly from the values calculated theoretically. The discrepancy is almost constant at 1-1.3 units.

The compounds numbered 2 and 7 in the table were tested on corn weevils for insecticidal activity, but this was found to be very low.

TABLE

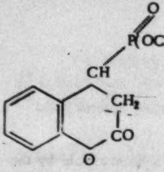
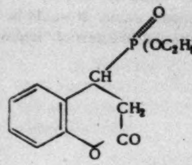
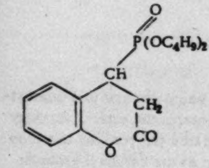
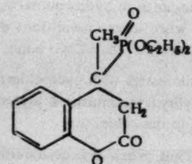
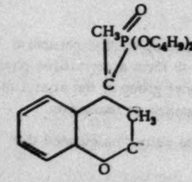
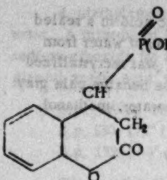
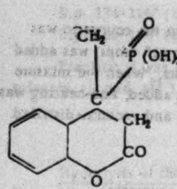
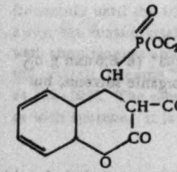
Formula	B.p. in °C (p in mm)	d_0^{20}	n_D^{20}	MR		Yield (%)
				Found	Calculated	
	190-195 (7)	1.3038	1.5303	60.70	59.71	19.6
	200-203 (6-6.5)	1.2255	1.5150	60.91	68.93	17
	223 (7-7.5)	1.1302	1.5015	88.75	87.42	18.3
	196-198 (5)	1.2131	1.5205	74.77	73.57	24
	215-218 (5-5.5)	1.1273	1.5070	93.42	92.14	24.3

TABLE (Continued)

Formula	B.p. in °C (p in mm)	d_0^{20}	n_D^{20}	MR		Yield (%)
				Found	Calculated	
	M.p 218-220°(from a mixture of ethyl and butyl acetates)					
	M.p 192-193 (colorless needles from ethyl acetate)					
	M.p 146-149°					

We carried out some experiments on the reaction of diethyl phosphorodithioate with coumarin. but no positive results were obtained. It was evident that reaction did occur under certain conditions, but we were unable to isolate an individual product because decomposition occured during distillation at reduced pressure (10-14mm). Positive resul were again not obtained for the reaction of diethyl phosphite with 2,6-dimethyl-4H-pyran-4-one, no addition products being obtained under similar reaction conditions.

EXPERIMENTAL

1. Reaction of Dimethyl Phosphite with Coumarin

Equivalent amounts of coumarin (5.8 g) and dimethyl phosphite (4.4 g) were placed in an Arbuzov flask. The dissolution of the coumarin in the dimethyl phosphite was accompanied by a fall in temperature from 19° to 15°. After the addition of ten drops of a concentrated solution of sodium methoxide in methanol, almost the whole of the coumarin dissolved and formed a clear solution.. This solution was heated in an oil bath at 110-120° for 20 hours. The product was a thick liquid having the color of weak tea. Vacuum distillation after the addition of a few drops of glacial acetic acid gave the following fractions:

B.p. 65-72° (15 mm); 2 g
B.p. 135-155°(7mm) 2 g (solidified in the condenser)
B.p. 155-195°(7mm); 2.8 g

Redistillation of Fraction III gave the fractions:

B.p. 143-190°(7mm); 0.3 g
B.p. 190-195°(7mm); 2 g(19.6%)

The second of these fractionswas investigated in greater detail and found to have n_D^{20} 1.5303; d_4^{20} 1.3038; found MR 60.70; calculated MR 59.71. It was a very viscous liquid, soluble in benzene and ether, but insoluble in water.

Found %: P 11.63

$C_{11}H_{13}O_5P$. Calculated %: P 12.10

Hydrolysis of the Product. The product (0.8 g) was heated with 10 ml of 1 : 1 hydrochloric acid in a sealed tube at 100° for five hours. The contents of the tube were evaporated on a water bath with addition of water from time to time until the hydrochloric acid had been completely removed. The crystalline product was recrystallized from a 1:4 mixture of ethyl and butyl acetates. Fine colorless needles were obtained, and these became pale gray when heated to 200°, and then melted to a brown liquid at 218-220°. The substance is soluble in water, methanol, ethanol, acetone, and acetic esters.

Found %: P. 13.08

$C_9H_9O_5P$. Calculated %: P 13.59

2. Reaction of Diethyl Phosphite with Coumarin

Reaction was between 7 g of coumarin (m.p. 68-70°) and 7.4 g of diethyl phosphite. When the coumarin was added to the diethyl phosphite, slight cooling (by 2-3°) was observed. Sodium ethoxide solution (10 drops) was added (there was no rise of temperature), and the mixture was heated in an oil bath at 120° for six hours. When the mixture was cooled, coumarin crystals were precipitated. More sodium ethoxide solution (10 drops) was added, and heating was continued at 125-135° for six hours. The mixture was then neutralized with glacial acetic acid and vacuum-distilled. The fractions obtained were:

B.p. 67-71° (10 mm); 3.6 g
B.p. 145-155° (10 mm); 3.0 g (solidified in the condenser; it was found to be unchanged coumarin)
B.p. 165-198° (4.5 mm); 4.2 g
Residue in flask 3 g

Refractionation of Fraction III yielded 2.5 g (about 17%) of a substance having b.p. 200-203° (6-6.5 mm); n_D^{20} 1.5150; d_4^{20} 1.2255; Found MR 69.91; Calculated MR 68.93. It was a colorless oil, soluble in organic solvents, but insoluble in water.

Found % P 11.03; 11.39

$C_{13}H_{17}O_5P$. Calculated %: P 10.91

Analysis indicated that the substance was the product formed by the addition of one molecule of diethyl phosphite to one molecule of coumarin.

Hydrolysis of the Product. A sealed tube containing 1 g of the product and 10 ml of 1:1 hydrochloric acid was heated in a boiling water bath for 6 hours 30 minutes. Evaporation of water and removal of hydrochloric acid on a water bath left a crystalline substance (about 1 g), which was dirty pink in color. It was recrystallized from a mixture of ethyl and butyl acetates, the solutions being treated with activated charcoal. The pure acid melted at 218-220°.

3. Reaction of Dibutyl Phosphite with Coumarin

A mixture of 3.5 g of coumarin and 4.7 g of dibutyl phosphite was prepared in an Arbuzov flask, when dissolution occured with a fall in temperature of 3°. After the addition of 8-10 drops of a saturated solution of sodium butoxide in butyl alcohol, the mixture was heated for 6.5 hours at 130-140° and for 10 hours at 145-155°. The contents of the flask then consisted of a viscous liquid having the color of weak tea. The material was neutralized with glacial acetic acid and vacuum-distilled. The fractions obtained were:

B.p. 108-132° (8 mm); 2.4 g (mixture of original substances)
B.p. 132-145° (8 mm); 1.1 g (solidified in condenser; mainly coumarin)
B.p. 223° (7-7.5 mm); 1.5 g (18.3%)

Fraction III, a thick yellowish liquid, was similar in properties to the product of the preceding experiment; it had n_D^{20} 1.5015; d_4^{20} 1.1302; Found MR 88.75; Calculated MR 87.42.

Found %: P 9.52; 9.58

$C_{17}H_{25}O_5P$. Calculated %: P 9.11

Hydrolysis of the Product. The product (0.7 g) was refluxed with 10 ml of 1:1 hydrochloric acid for three hours. After the usual treatment, the hydrolysis product was recrystallized from a 4:1 mixture of ethyl and butyl acetates. Colorless crystals were obtained which were identical with those obtained previously by hydrolysis of the addition products formed by dimethyl phosphite and by diethyl phosphite with coumarin (m.p. 218-220°; mixture test, m.p. 218-219.5°).

4. Reaction of Diethyl Phosphite with 4-Methylcoumarin

4-Methylcoumarin was prepared, as previously described [6], by the condensation of phenol with acetoacetic ester. A mixture of 9 g of 4-methylcoumarin and 7.7 g of diethyl phosphite was heated with 10 drops of alcoholic sodium ethoxide for six hours in a water bath and then for four hours at 120-125°. After the addition of a few drops of glacial acetic acid, the mixture was vacuum-fractionated and yielded:

B.p. 65-68° (9 mm); 4.3 g
B.p. 160-172° (5mm); 2.3 g (solidified in condenser; methylcoumarin)
B.p. 172-200° (5mm); 7 g

There was a thick brown resinous residue. Fraction III was redistilled and yielded:

B.p. 174-196° (5 mm); in very small amount
B.p. 196-198° (5 mm); (with slight decomposition)

Fraction II was a thick oil, insoluble in water, but readily soluble in ether, benzene, acetone, and other organic solvents. It had n_D^{20} 1.5205; d_4^{20} 1.2131; Found MR 74.77; Calculated MR 73.57. The yield was 4 g (24%).

Found %: P 10.55; 10.35
$C_{14}H_{19}O_5P$. Calculated %: P 10.39

Hydrolysis of the Product. A sealed tube containing 2 g of the product and 15 ml of 1:1 hydrochloric acid was heated for six hours in a water bath. The contents of the tube were evaporated on the water bath, water being added frequently until the whole of the hydrochloric acid had been removed. When the whole of the water was evaporated away, the mass crystallized, 1.9 g of dirty-red crystals being obtained. After two crystallizations from acetic acetate with simultaneous application of activated charcoal, colorless needles having a double melting point were obtained: the crystals became "wet" when heated to 108-110°, resolidified when heated further (120-125°), and finally melted at 192-193°. The substance is soluble in water and in alcohol, and it dissolves when heated with ethyl or butyl acetate or with acetone; it is sparingly soluble in benzene and ether, and is insoluble in petroleum ether.

Found %: P 12.56; 12.60
$C_{10}H_{11}O_5P$. Calculated %: P 12.80

5. Reaction of Dibutyl Phosphite with 4-Methylcoumarin

A mixture of 3.2 g of 4-methylcoumarin and 3.88 g of dibutyl phosphite was heated at 135-140° with a few drops of a solution of sodium butoxide in butyl alcohol for 6 hours 30 minutes. After the addition of 5-6 drops of glacial acetic acid, the product was vacuum-distilled. After a second distillation 1.7 g (24.3%) of a fraction boiling with slight decomposition at 215-218° (5-5.5 mm) was obtained. It had n_D^{20} 1.5070; d_4^{20} 1.1283; Found MR 93.42; Calculated MR 92.14. It was a viscous liquid, soluble in organic solvents.

Found % P 8.26
$C_{18}H_{27}O_5P$. Calculated %: P 8.75

Hydrolysis of the Product. The product (0.7 g) was refluxed with 10 ml of 1:1 hydrochloric acid until the oil present disappeared (three hours). Evaporation on a water bath yielded a solid substance, which was crystallized from ethyl acetate (colorless needles). Its melting point was not depressed by admixture of the product of the hydrolysis of the corresponding ethyl ester.

6. Reaction of Diethyl Phosphite with Acetylcoumarin

Acetylcoumarin (m.p. 123°, from alcohol) was prepared by the condensation of salicylaldehyde with acetoacetic ester in presence of piperidine [7]. A mixture of equimolecular amounts of acetylcoumarin (9 g) and diethyl phosphite (6.6 g) with 8 drops of a saturated alcoholic solution of sodium ethoxide was heated in an Arbuzov flask in an oil bath at 120°. After two hours the flask was cooled, when its contents solidified completely to a very dense brown mass (in order to remove it it was necessary to break the flask). The product was recrystallized from absolute methanol with the application of activated charcoal, and crystals melting at 146-149° were obtained. We did not succeed in obtaining crystals having a sharper melting point, probably owing to the occurrence of transesterification during crystallization from methanol. When the product was melted it would not resolidify, but remained as a viscous liquid. The use of other solvents for the purpose of crystallization did not give the desired results. The substance was soluble in hot alcohol and slightly soluble in hot water; it was readily soluble in benzene and ethyl acetate, but insoluble in petroleum ether.

Found %: P 9.85; 9.74

$C_{15}H_{19}O_6P$. Calculated %: P 9.50

An attempt to prepare the phenylhydrazone by the action of phenylhydrazine in glacial acetic acid did not give positive results, though, under the same conditions, pure acetylcoumarin readily gave a phenylhydrazone, m.p. 182-183°.

Hydrolysis of the Product. The substance (2 g) was refluxed with 18 ml of 1 : 1 hydrochloric acid for three hours. The clear solution was evaporated in a dish on a water bath until the hydrochloric acid was removed completely. When cooled, the contents of the dish solidified to a very hard glossy mass, which we were unable to recrystallize in spite of attempts with all of the usual solvents. The product was ground in a mortar, when it formed a dirty-violet powder. It did not change when heated to 125°, and then turned red as the temperature was raised further.

Found % P 12.03; 12.05

$C_{11}H_{11}O_6P$. Calculated %: P 11.47

7. Experiments with Hydrocoumarin

Hydrocoumarin was prepared by the reduction of coumarin with sodium amalgam and distillation of the melilotic acid obtained [8]. It had b.p. 269-271° and n_D^{20} 1.5595; the literature gives b.p. 272°. Dihydrocoumarin was identified by the preparation of its dibromide, m.p. 104-106° (the literature gives 106°).

Experiment 1. A mixture of 5 g of hydrocoumarin and 4.65 g of diethyl phosphite was heated in an Arbuzov flask with 10 drops of sodium ethoxide solution at 125-135° for 17 hours. After three fractionations the original substances were recovered. No high-boiling fractions were detected.

Experiment 2. A mixture of 9.7 g of hydrocoumarin and 9.04 g of diethyl phosphite was heated with 15 drops of sodium ethoxide solution at 150-155° for 10.5 hours. After several fractionations 7.5 g of diethyl phosphite (b.p. 75-80°/14 mm) and 6.7 g of hydrocoumarin (b.p. 268-272°; n_D^{20} 1.5590) were obtained. There was a very small amount of thick brown resinous residue in the distillation flask.

8. Experiments with 2,6-Dimethyl-4H-pyran-4-one

Experiment 1. A mixture of equimolecular amounts of 2,6-dimethyl-4H-pyran-4-one (4.4 g) and diethyl phosphite (4.9 g) was heated in a water bath with 12-15 drops of a saturated solution of sodium ethoxide for 7.5 hours. When the mixture was cooled, crystals of the pyrone came down. The mixture was heated further for 14 hours at 130°. The contents of the flask then consisted of a thick brown resinous liquid, the distillation of which yielded:

B.p. 75-80° (10 mm); 2.5 g
B.p. 80-125° (10-14 mm)

Fraction II partially crystallized out, and 1.8 g of 2,6-dimethyl-4H-pyran-4-one was obtained. When the temperature was raised further, decomposition set in and the pressure rose to 16 mm. In the distillation flask there remained a glossy black carbonaceous product (2 g) reminiscent of anthracite.

Experiment 2. A mixture of 4.85 g of 2,6-dimethyl-4H-pyran-4-one and 5.4 g of diethyl phosphite was heated with 12 drops of sodium ethoxide solution at 110-120° for the duration of four daily sessions (about 30 hours). When the mixture was cooled, crystals of the pyrone came down (2.8 g; m.p. 131-132°). Vacuum distillation gave:

B.p. 68-78° (8-7.5 mm); 4 g n_D^{20} 1.4075 (impure diethyl phosphite)
B.p. 108-115 (8-7.5 mm); in small amount (2,6-dimethyl-4H-pyran-4-one)

There was a black residue in the flask. The reaction did not go.

9. Reaction of Diethyl Phosphorodithioate with Coumarin

Experiment 1. A mixture of 4.1 g of diethyl phosphorodithioate and 3.1 g of coumarin was heated in a water bath for six hours. When the reaction mixture was cooled, yellow crystals came down, and these were found to be coumarin contaminated with sulfur (m.p. 68-70°). An addition of 10 drops of sodium ethoxide solution was made, and heating was continued for a further six hours. Fractionation of the mixture under reduced pressure yielded the original substances; there were no high-boiling fractions. The reaction did not go.

Experiment 2. A mixture of 7.3 g of coumarin, 9.3 g of diethyl phosphorodithioate, and 15 ml of dry benzene was heated in a sealed tube at 120-125° for seven hours. The tube was found to contain an intensely black liquid, which was fractionated. The products isolated were 3 g of diethyl phosphorodithioate, b.p. 109-112° (9 mm). and 4 g of a fraction boiling at 145-148° (9 mm), which solidified in the condenser to yellow crystals (coumarin contaminated with sulfur). Further heating resulted in decomposition. There was a resinous residue.

Experiment 3. A mixture of 7.3 g of coumarin and 9.3 g of diethyl phosphorodithioate was refluxed at 150° for 15 minutes. The contents of the flask became yellow. Distillation yielded 1.5 g of a fraction having b.p. 37-42° and n_D^{20} 1.4368, which correspond to ethanethiol (reported values: b.p. 37°, n_D^{20} 1.4305). Further distillation under reduced pressure gave the following fractions:

B.p. 115-126° (14 mm) a small amount of diethyl phosphorodithioate.
B.p. 126-152° (14 mm); yellow liquid, which partially crystallized, yielding coumarin, m.p. 67-69°.
B.p. 152-155° (14 mm); 1.3 g coumarin.

At the end of the distillation decomposition set in. Much resin remained in the distillation flask.

SUMMARY

1. In presence of sodium alkoxides, dialkyl phosphites add to coumarin and to 4-methylcoumarin with formation of esters of hydrocoumarin-4-yl- and 4-methylhydrocoumarin-4-yl-phosphonic acids, respectively.

2. Experiments on the addition of diethyl phosphite to 2,6-dimethyl-4H-pyran-4-one and of diethyl phosphorodithioate to coumarin did not give positive results.

Received June 18, 1954

A. M. Butlerov Chemical Research Institute
of the Ulyanov-Lenin Kazan University

LITERATURE CITED

[1] B. A. Arbuzov and B. P. Lugovkin, J. Gen. Chem. 21, 1869 (1951) (T.p. 2075).*

[2] B. A. Arbuzov and B. P. Lugovkin, J. Gen. Chem. 22, 1193 (1952) (T.p. 1241).*

[3] B. A. Arbuzov and B. P. Lugovkin, J. Gen. Chem. 22, 1199 (1952) (T.p. 1247).*

[4] B. A. Arbuzov and V. M. Zoroastrova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No. 5, 806 (T.p. 697)*.

[5] B. A. Arbuzov and A. N. Pudovik, Bull. Acad. Sci USSR, Div. Chem. Sci. 1949, 522.

[6] See Synthesis of Organic Substances 3, 1952, p. 305.

[7] E. Knoevenagel, Ber. 31, 732 (1898).

[8] R. Fittig, Ann. 226, 356 (1884).

---

* T. p. = C. B. Translation pagination.

BLANK
PAGE

REACTIONS OF MERCAPTO AMINO ACIDS

COMMUNICATION 9. SYNTHESIS OF α-ACYLAMINO β-THIOLACTONES

I. L. Knunyants, O. V. Kildisheva, and E. Ya. Pervova

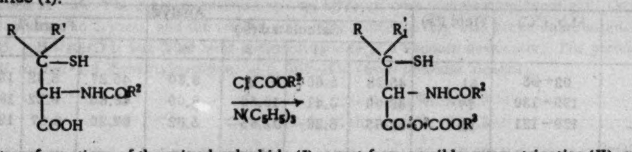
In spite of the great progress that has been made in the synthesis of polypeptides having a predetermined sequence of amino-acid residues, there are still great difficulties in the way of the preparation of mixed polyamides in which the chain is built up from mercapto amino acids as well as the usual α-amino acids. Only very few such polypeptides have been synthesized. Still less study has been devoted to polypeptides derived entirely from mercapto amino acids. The following are known: L-cystyl-L-cystine, prepared by the hydrolysis of the corresponding piperazinedione [1]; polycystine, prepared by heating L-cystine bis-N-carboxyanhydride [2]; poly-S-benzylcysteine [3] prepared from S-benzyl-L-cysteine N-carboxyanhydride; and L-methionyl-L-methionine and L-methionyl-L-methionyl-L-methionine, prepared by the azide method from N-(benzyloxycarbonyl) methionine [4].

The only known dipeptide containing free thiol groups is cysteinylcysteine. Polypeptides derived from 3,3-dimethylcysteine and other mercapto amino acids have not been studied.

Complications arise in the synthesis of such polypeptides owing to the high reactivity of mercapto amino acids, in which not only the amino, but also the thiol groups must be blocked before the compounds can be applied in the peptide synthesis. The removal of the protective groups from the resulting polypeptides can be effected only with difficulty. The usual method of blocking a thiol group is benzylation, and the benzyl group may be removed from the polypeptide by reduction with sodium in liquid ammonia. As shown in the preceding communications, in the case of 3,3-dimethylcysteine blocking the amino groups (acylation) presents no difficulty and can be readily carried out even without previous protection of the thiol group [5].

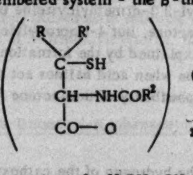
Among the general methods of synthesizing peptides (from piperazinediones, acid chlorides, azides, etc.), the one most widely applied in recent times is the method of acylation with the aid of mixed anhydrides and N-carboxyanhydrides of amino acids, and most frequently mixed anhydrides of acylamino acids with carbonic monoesters are used. An illustration of the possibilities of this method is provided by the synthesis of cyclo-D-leucylglycylglycine in 37 % yield [6], and also by the synthesis of a cyclic octapeptide [7], which was found to be identical in its chemical and physical properties with the natural hormone oxytocin.

The application of this method to mercapto acylamino acids must inevitable lead to the formation of the mixed anhydride (I):

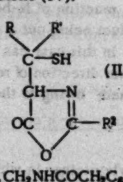


(1)

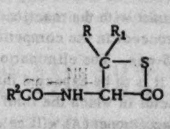
The further transformations of the mixed anhydride (I), apart from possible symmetrization (II), may proceed in two competing directions, with formation of a five-membered system – the oxazolinone (III), and with formation of a four-membered system - the β-thiolactone (IV):



(II)



(III)

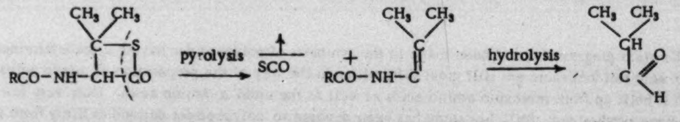


(IV)

$R^2 = H, CH_3, CH_2C_6H_5, CH_2NHCOCH_2C_6H_5$

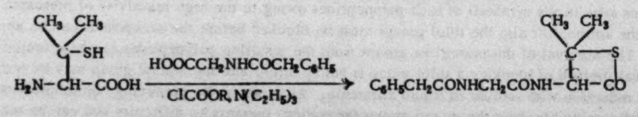
Investigation showed that N-acyl-3,3-dimethylcysteines readily react with chloroformic ester in anhydrous solvents in presence of bases, and even at − 5° the ferric chloride reaction for a thiol group ceases to be given *. When the temperature is raised to that of the room, vigorous evolution of carbon dioxide occurs.

The readily crystallizing substances obtained by the reaction correspond in analysis to products of the dehydration of N-acyldimethylcysteines, and do not contain a thiol group (negative reaction with iodine; infrared-spectrum evidence). When decomposed by heat they lose carbonyl sulfide and form a 2-methylpropenylamide, which yields isobutyraldehyde when subsequently hydrolyzed:



These compounds, therefore, are α-acylamino β-thiolactones—derivatives of the new class of β-thiolactones recently prepared by Linkova, Kildisheva, and Knunyants [8].

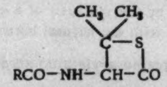
We have here yet another example of the readiness with which four-membered rings are formed. Thiolactones of this type were prepared from N-formyl-, N-acetyl-, N-phenylacetyl-, and N-phenaceturyl-3,3-dimethylcysteines (see the table). It was found also that a thiolactone could be prepared in one stage. For example, the direct acylation of 3,3-dimethylcysteine with the mixed anhydride of phenaceturic acid and a monoester of carbonic acid in presence of an excess of chloroformic ester yields the corresponding thiolactone:



If it is required to arrest the reaction at the stage of the formation of 3,3-dimethyl-N-phenaceturylcysteine, that it is essential to use the strictly equivalent amount of chloroformic ester necessary for the formation of the ester of the phenaceturic-carbonic anhydride. Under these conditions, 3,3-dimethyl-N-phenaceturylcysteine can be obtained in 70% yield.

TABLE

N-Acyl-3,3-dimethylcysteine β-Thiolactones

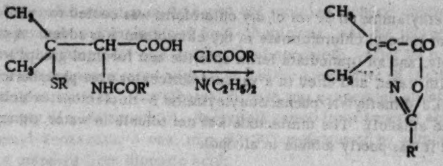


No.	R	M.p. (°C)	Yield (%)	Analysis							
				Calculated (%)				Found %			
				C	H	S	N	C	H	S	N
1	H—	93—96	51	45.28	5.66	20.12	8.80	45.27	5.42	19.86	8.98
2	CH_3—	129—130	77	48.00	6.41	18.50	8.09	48.80	6.22	18.18	8.16
3	$C_6H_5CH_2$—	129—131	99	62.65	6.26	12.85	5.62	62.20	6.07	12.62	5.60
4	$C_6H_5CH_2CO$— $NHCH_2$—	194—195	99	58.82	5.88	10.45	9.15	59.10	5.80	10.61	9.22

In contrast with the reactions discussed above, the reaction of N-benzoyl-3,3-dimethylcysteine under the same conditions proceeds in the competing direction, the product being not a thiolactone, but 4-isopropylidene-2-phenyl-2-oxazolin-5-one. The elimination of hydrogen sulfide in this case can be explained by the formation of a conjugated system. It is to be expected that this will be the main direction of reaction when acid halides act on mercapto acylamino acids in which the thiol group has been blocked; owing to the impossibility of thiolactone formation, unsaturated oxazolinones (A) will be obtained;

---

* It was previously established that N-acyl-3,3-dimethylcysteines in which the hydrogen of the carboxyl is blocked do not give the usual ferric chloride reaction for free thiol groups; in such cases the thiol group can be detected only by the iodine reaction [5].

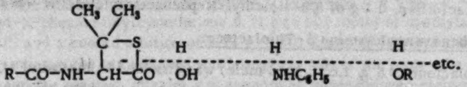


(A)

R = CH_3, $C_6H_5CH_2$;
R' = C_6H_5, $C_6H_5CH_2$, $C_6H_5CH_2CONHCH_2$

Thus, from N-benzoyl-S-benzyl-, S-benzyl-N-phenylacetyl-, and S-methyl-N-phenaceturyl-3,3-dimethylcysteines, the corresponding unsaturated oxazolinones were prepared by the action of chloroformic ester in presence of trimethylamine.

A study of the properties of thiolactones showed that these compounds are stable: their hydrolysis by water proceeds very slowly at room temperature, only 50% of the thiolactone being converted into the N-acyl-3,3-dimethylcysteine in the course of two weeks. When warmed with water or bicarbonate solution, thiolactones are readily hydrolyzed to the corresponding acids, and the solution then again gives the ferric chloride reaction for the thiol group. When thiolactones are heated with alcohols, esters of N-acyl-3,3-dimethylcysteine are formed. They react with aniline even at room temperature, with formation of analides. Alcoholysis in presence of lead acetate yields the corresponding mercaptides:



EXPERIMENTAL

General Method for the Preparation of β-Thiolactones from N-Acyl-3,3-dimethylcysteines. A solution of one molecular proportion of the N-acyl-3,3-dimethylcysteine and two molecular proportions of triethylamine in dry chloroform was cooled to −10° and stirred while a cooled solution of 1.5 molecular proportions of isobutyl chloroformate in dry chloroform was added (the temperature must not be allowed to rise above −6°). The reaction mixture was kept at −6° until there was no longer a reaction for the thiol group (5-10 minutes), and the temperature was then allowed to rise to that of the room (there was a vigorous evolution of carbon dioxide, even at 0°). The solution was evaporated under reduced pressure, the dry residue was rubbed out with ether, and the substance was filtered off, washed well with water, dried in a vacuum desiccator over phosphoric oxide, and crystallized.

Anilide of N-Formyl-3,3-dimethylcysteine. The above-described preparation was carried out on 0.17 g (0.001 mole) of N-formyl-3,3-dimethylcysteine up to the stage of the disappearance of the reaction for the thiol group with ferric chloride and, without isolation of the thiolactone, a solution of 0.09 g (0.001 mole) of aniline in dry chloroform was then added at −5°. The reaction mixture was set aside at room temperature overnight. On the next day the solution was evaporated to dryness and the residue was washed successively with bicarbonate solution, water, dilute hydrochloric acid, and water. It was dried over phosphoric oxide in a vacuum desiccator. The product was 0.1 g of the anilide of N-formyl-3,3 dimethylcysteine. m.p. 165-169° (from absolute alcohol).

Found%: N 11.3
$C_{12}H_{16}O_2N_2S_2$. Calculated%: N 11.3

Anilide of N-Acetyl-3,3-dimethylcysteine. A solution of 0.25 g (0.0014 mole) of N-acetyl-3,3-dimethylcysteine β-thiolactone in 0.5 g (0.005 mole) of aniline was prepared. The solution was set aside at room temperature overnight, and on the next day the precipitate that had formed was filtered off and washed successively with 2 N HCl, water, bicarbonate solution, and again water. The product was 0.38 g (a quantitative yield) of the anilide of N-acetyl-3,3-dimethylcysteine, m.p. 193-195° (from alcohol).

Found%: C 58.45; H 6.80; S 11.92; N 10.71
$C_{13}H_{18}O_2N_2S$. Calculated%: C 58.64; H 6.76; S 12.03; N 10.52

3,3-Dimethyl-N-phenaceturylcysteine β-Thiolactone *. A solution of 0.97 g (0.003 mole) of 3,3-dimethyl-

---

* The first suggestion that a β-thiolactone is formed in the reaction of acetic anhydride with 3,3-dimethyl-N-phenaceturylcysteine was made by Sus[9], but the substance that he isolated melted at 143°.

N-phenaceturylcysteine and 0.6 g (0.006 mole) of triethylamine in 20 ml of dry chloroform was cooled to −10° and stirred while a cooled solution of 0.4 g (0.003 mole) of isobutyl chloroformate in dry chloroform was added. A copious precipitate of the thiolactone formed immediately, and an immediate ferric chloride test for thiol groups was negative. The precipitate was filtered off, washed with water, and dried in a vacuum desiccator over phosphoric oxide. The product was 0.9 g (a quantitative yield) of 3,3-dimethyl-N-phenaceturylcysteine β-thiolactone, which melted with decomposition at 191-194° (from absolute ethanol). The thiolactone was not soluble in water, ether, chloroform, benzene, ethyl acetate, and dioxane, and it was poorly soluble in alcohol.

Found %: C 59.1; H 5.80; S 10.60; N 9.20

$C_{15}H_{18}O_3N_2S$. Calculated %: C 58.82; H 5.88; S 10.45; N 9.15

b) A solution of 0.62 g (0.003 mole) of phenaceturic acid and 0.3 g (0.003 mole) of triethylamine in 10 ml of dry chloroform was cooled to −10° and stirred while 0.84 g (0.006 mole) of isobutyl chloroformate was added. After 5-10 minutes a cooled solution of 0.45 g (0.003 mole) of 3,3-dimethylcysteine in 3 ml of N NaOH (0.002 mole) was added, and the mixture was stirred vigorously with cooling for 15 minutes (a copious precipitate of thiolactone formed); stirring was continued for a further 30 minutes at 20°. The precipitate was filtered off, washed with chloroform, and dried in a vacuum desiccator over phosphoric oxide. The product was 0.45 g (50%) of 3,3-dimethyl-N-phenaceturylcysteine β-thiolactone, m.p. 170-181°, raised by recrystallization from alcohol to 190-192°. A mixture test with the substance obtained in the preceding experiment showed no depression.

When the alkaline solution was acidified, 0.1 g of 3,3-dimethyl-N-phenaceturylcysteine was obtained.

Reactions of 3,3-Dimethyl-N-phenaceturylcysteine β-Thiolactone.

a) With lead acetate. The thiolactone (0.5 g, i.e. 0.0016 mole) was dissolved in methanol at 40° and 0.5 g (0.0015 mole) of lead acetate was added. The mixture was refluxed for eight hours, and the black precipitate formed was filtered off (60 mg, i.e. 15%, of lead sulfide). The filtrate was evaporated under reduced pressure at room temperature. The yellow residue was well washed with ether, alcohol, and then water; it was dried over phosphoric oxide in a vacuum desiccator. The product was 0.5 g of the methyl ester of 3,3-dimethyl-N-phenaceturylcysteine in the form of its lead mercaptide. Evaporation of the ether-alcohol mother liquor yielded a further 0.1 g of the mercaptide. The total yield of mercaptide was 0.6 g (85%). It was crystallized from dioxane and then from absolute alcohol. After being dried over phosphoric oxide in a vacuum, it melted with decomposition at 150° (partial liquefaction occurred at 110°).

Found %: C 43.57; H 4.94; N 5.80; CH_3O 7.52

$C_{32}H_{42}O_8N_4S_2Pb$. Calculated %: C 43.58; H 4.76; N 6.35; CH_3O 7.03

b) Pyrolysis. 3,3-Dimethyl-N-phenaceturylcysteine β-thiolactone was heated at a temperature close to its melting point (190°) at a residual pressure of 2 mm for 20-30 minutes (until decomposition ceased). The residue was rubbed out with ether and recrystallized from ethyl acetate.

The product was a crystalline substance melting at 157-158° (N-2-methylpropenylphenaceturamide).

Found %: C 68.18; H 7.42; N 11.22

$C_{14}H_{18}N_2O_2$. Calculated %: C 68.29; H 7.32; N 11.38

In order to prove that this was N-2-methylpropenylphenaceturamide, it was hydrolyzed with 2 N HCl in presence of 2,4-dinitrophenylhydrazine. The precipitate that formed was filtered off and crystallized from alcohol. The product was a hydrazone melting at 178-180°, and there was no depression in a mixture test with the 2,4-dinitrophenylhydrazone of isobutyraldehyde.

4-Isopropylidene-2-phenyl-2-oxazolin-5-one.

a) From N-benzoyl-3,3-dimethylcysteine. A solution of 0.54 g (0.002 mole) of N-benzoyl-3,3-dimethylcysteine and 0.4 g (0.004 mole) of triethylamine in 5 ml of dry chloroform was cooled to −10°, and a cooled solution of 0.28 g (0.002 mole) of isobutyl chloroformate was added. After 15 minutes the temperature was raised to that of the room and the solution was evaporated to dryness. The residue was extracted with ether; the yield of $HCl\cdot N(C_2H_5)_3$ was quantitative. The ether solution was evaporated at room temperature, and the oily residue was treated with a small amount of alcohol. The product was 0.28 g (70%) of 4-isopropylidene-2-phenyl-2-oxazolin-5-one, m.p. 94-95°, undepressed by admixture of 4-isopropylidene-2-phenyl-2-oxazolin-5-one prepared by another method.

b) From N-benzoyl-S-benzyl-3,3-dimethylcysteine. A solution of 0.34 g (0.001 mole) of N-benzoyl-S-benzyl-3,3-dimethylcysteine and 0.1 g (0.001 mole) of triethylamine in 5 ml of dry chloroform was cooled to −10°, and a cooled solution of 0.14 g (0.001 mole) of isobutyl chloroformate in dry chloroform was added. The same temperature was maintained for 5-10 minutes, and the temperature was then raised gradually to that of the room (at 0° the sharp odor of α-toluenethiol appeared). After 20 minutes the solution was evaporated in the air. The oily residue was treated with ether, and the precipitate of triethylamine hydrochloride was filtered off (the yield was quantitative). The ethereal filtrate was evaporated under reduced pressure. The dry residue (0.25 g) smelled strongly of α-toluenethiol. Recrystallization from aqueous acetone yielded 0.14 g (70%) of 4-isopropylidene-2-phenyl-2-oxazolin-5-one, m.p. 93-96°, undepressed by admixture of 4-isopropylidene-2-phenyl-2-oxazolin-5-one prepared from hippuric acid.

S,3,3-Trimethyl-N-phenaceturylcysteine. A solution of 0.42 g (0.003 mole) of methyl iodine in 5 ml of ethanol was added to a solution of 0.96 g (0.003 mole) of 3,3-dimethyl-N-phenaceturylcysteine in 8 ml of N NaOH (0.003 mole). The ferric chloride reaction for the thiol group disappeared immediately. Alcohol was removed under reduced pressure at room temperature. The alkaline aqueous solution that remained was extracted with ether, acidified to Congo red with concentrated hydrochloric acid, and left in a refrigerator for several hours. The crystalline precipitate was filtered off, washed with water, and dried. The product was 0.6 g (60%) of S,3,3-trimethyl-N-phenaceturylcysteine, m.p. 115-117° (from a 1:3 mixture of benzene and ethyl acetate).

Found %: C 56.82; H 6.52; S 9.59

$C_{16}H_{22}O_4N_2S$. Calculated %: C 56.80; H 6.50; S 9.46

4-Isopropylidene-2-(phenylacetamidomethyl)-2-oxazolin-5-one. A solution of 0.34 g (0.001 mole) of S,3,3-trimethyl-N-phenaceturylcysteine and 0.11 g (0.001 mole) of triethylamine in 5 ml of dry chloroform was cooled to −10°, and a cooled solution of 0.14 g (0.001 mole) of isobutyl chloroformate in dry chloroform was added. After five minutes the temperature was brought to that of the room (the evolution of methanethiol was observed already at 0°) and the reaction mixture was evaporated under reduced pressure. The oily residue solidified when rubbed out with absolute ether. The substance was filtered off, washed with water, and dried over phosphoric oxide in a vacuum desiccator. The product was 0.25 g (a quantitative yield) of 4-isopropylidene-2-(phenylacetylamidomethyl)--2(phenylacetylamidomethyl)-2-oxazolin-5-one, m.p. 121-122° (from absolute alcohol). This oxazolinone is readily soluble in ethyl acetate and alcohol, but insoluble in ether and in water.

Found %: C 65.72; H 6.03; N 10.49

$C_{15}H_{16}O_3N_2$. Calculated %: C 66.17; H 5.89; N 10.3

SUMMARY

1. When treated with chloroformic esters, N-acyl-3,3-dimethylcysteines give N-acyl-3,3-dimethylcysteine β-thiolactones in excellent yield. N-Benzoyl-3,3-dimethylcysteine is an exception, and under the same conditions it loses hydrogen sulfide and is converted into 4-isopropylidene-2-phenyl-2-oxazolin-5-one.

2. When the new thiolactones prepared in this way are treated with aniline, they yield the corresponding N-acyl-3,3-dimethylcysteine anilides.

3. When N-acyl-S-alkyl (or aralkyl)-3,3-dimethylcysteines are treated with chloroformic esters, the elimination of thiols readily occurs, and 2-alkyl (or aralkyl)-4-isopropylidene-2-oxazolin-5-ones are formed.

Received October 15, 1954

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

LITERATURE CITED

[1] J. Greenstein J. Biol. Chem. 121, 9 (1937).

[2] H. Jones, H. P. Lundgren, J. Am. Chem. Soc. 73, 5465 (1951).

[3] E. P. Blakley, A. K. Sumner, Can. J. Technol. 30, 158 (1952).

[4] M. Brenner, K. Pfister, Helv. Chim. Acta. 24, 2085 (1951).

[5] I. L. Knunyants and M. G. Linkova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 1, 62, (T. p.53)*

[6] P. A. Boissonnas, J. Schumann. Helv. Chim. Acta. 35, 2229 (1952).

---

* T. p. = C. B. Translation pagination.

[7] V. du Vigneaud, C. Ressler, J. Swan et al., J. Am. Chem. Soc. 75, 4879 (1953).

[8] M. G. Linkova, O. V. Kildisheva, and I. L. Knunyants, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 3, 569. (T.p. 507)*

[9] O. Süs, Ann. 561, 31 (1948.

---

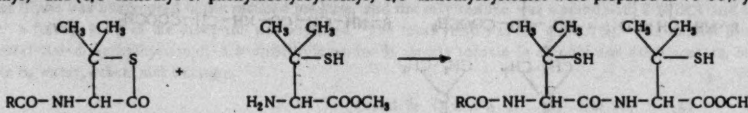
* T.p. = C. B. Translation pagination.

REACTIONS OF MERCAPTO AMINO ACIDS

COMMUNICATION 10. NEW METHOD FOR THE SYNTHESIS OF POLYPEPTIDES

I. L. Knunyants, O. V. Kilisheva, and E. Ya. Pervova

We have shown previously [1] that, under the action of dehydrating agents, N-acyl-3,3-dimethylcysteines are readily converted into thiolactones [1]. Further investigation of the properties of the new thiolactones has shown that they are just as reactive as mixed anhydrides of acylamino carboxylic acids, and by their aid we have succeeded in synthesizing di- and tri-peptides of 3,3-dimethylcysteine for the first time. The acylation of 3,3-dimethylcysteine can be carried out with isolated thiolactones, and can be effected also without their isolation in the pure state. In the second case the yield of dipeptide does not exceed 40-50%. By the acylation of the methyl ester of 3,3-dimethylcysteine in ethyl acetate solution at 20° with isolated thiolactones, (N-acetyl-3,3-dimethylcysteinyl)- and (3,3-dimethyl-N-phenylacetylcysteinyl)-3,3-dimethylcysteines were prepared in 70-80% yield:

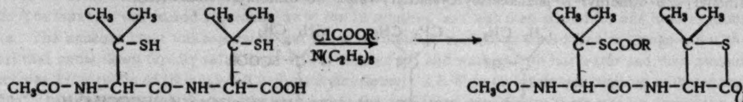


Like the esters of N-acyl-3,3-dimethylcysteine, the esters of N-acylated dipeptides of 3,3-dimethylcysteine do not give the ferric chloride thiol reaction. By hydrolysis with 2 N NaOH at 40-50° they are readily converted into the corresponding dipeptides in 60-70% yield.

The most convenient method for the preparation of single-component dipeptides was found to be the acylation of 3,3-dimethylcysteine with the isolated thiolactone in an aqueous alkaline medium at 25-35°. Dipeptides were obtained in yields of up to 80-90%. The acylation of various amino acids with thiolactones went just as readily and in excellent yield, and in this way the following mixed dipeptides were isolated: bis(3,3-dimethyl-N-phenylacetylcysteinyl) cystine, (3,3-dimethyl-N-phenylacetylcysteinyl) valine, and (N-formyl-3,3-dimethylcysteinyl) alanine. The dipeptides obtained were colorless crystalline compounds. The thiol groups of the mixed dipeptides could be detected only by the iodine reaction, owing to the blocking of the carboxyl of the dimethylcysteine. Further investigations showed that dipeptides of 3,3-dimethylcysteine are readily converted into thiolactones, which can then be used in the synthesis of more complex polypeptides.

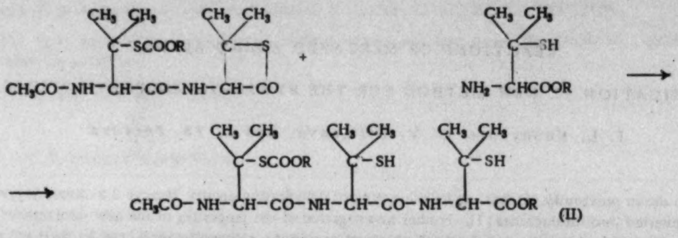
Thus, by the treatment of (N-acetyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine with a chloroformic ester in presence of triethylamine in an anhydrous medium, the acylamino thiolactone (I) was obtained.

The formation of the substance (I) was generally accompanied by simultaneous acylation of the free thiol group of the 3,3-dimethylcysteinyl residue:



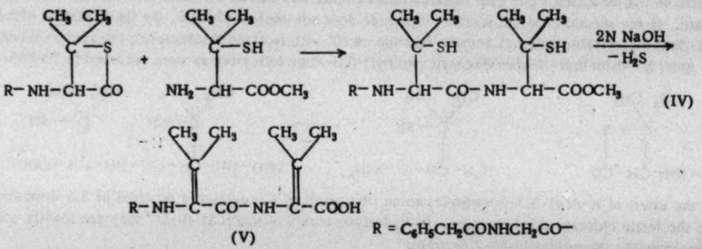
(I)

The thiolactone (I) is a stable crystalline compound, which is slowly hydrolyzed by aqueous solutions of caustic alkali. With aniline it readily forms the corresponding anilide, and with the methyl ester of 3,3-dimethylcysteine it forms the tripeptide methyl ester (II):



(II)

A mixed tripeptide was obtained by the acylation of the methyl ester of 3,3-dimethylcysteine with 3,3-dimethyl-N-phenaceturylcysteine β-thiolactone (III) under the same conditions:

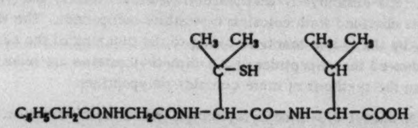


(IV)

(V)

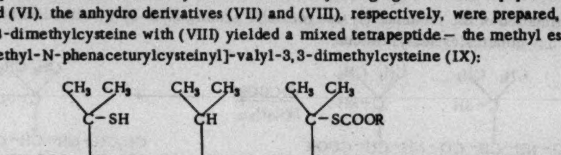
R = $C_6H_5CH_2CONHCH_2CO-$

Hydrolysis of the tripeptide methyl ester (IV) with alcoholic N NaOH at room temperature gave the tripeptide (3,3-dimethyl-N-phenaceturylcysteinyl)-3,3-dimethylcysteine. Hydrolysis of (IV) under more severe conditions (2 N NaOH at 40-50°) was accompanied by the elimination of two molecules of hydrogen sulfide and the formation of 3-methyl-2-(3-methyl-2-phenaceturaminocrotonamido) crotonic acid (V). Acylation of valine with the thiolactone (III) in an aqueous alkaline medium yielded the mixed tripeptide (3,3-dimethyl-N-phenaceturylcysteinyl) valine(VI):



(VI)

The mixed tripeptides were just as readily converted into acylating agents as the dipeptides were. Thus, from the tripeptides (IV) and (VI), the anhydro derivatives (VII) and (VIII), respectively, were prepared, and acylation of the methyl ester of 3,3-dimethylcysteine with (VIII) yielded a mixed tetrapeptide — the methyl ester of [S-(isobutoxycarbonyl)-3,3-dimethyl-N-phenaceturylcysteinyl]-valyl-3,3-dimethylcysteine (IX):



(IX)

There can be no doubt at all that the tetrapeptide (IX) will behave like the di- and tri-peptides of 3,3-dimethylcysteine under similar conditions and will give the corresponding anhydro derivative, by the aid of which it will be possible to obtain a pentapeptide. Our method, therefore, permits the preparation of single-component and mixed polyamides — the latter with a predetermined sequence of amino acids.

EXPERIMENTAL

(N-Formyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine. A solution of 0.9 g (0.005 mole) of N-formyl-3,3-dimethylcysteine and 1 g (0.01 mole) of triethylamine in 10 ml of dry chloroform was cooled to −10° and stirred while addition was made of a cooled solution of 0.65 g (0.005 mole) of isobutyl chloroformate in dry chloroform. The reaction mixture was allowed to stand at −6° until there was no longer a ferric chloride reaction for the thiol group (10 minutes). The mixture was then cooled to −10° and a cooled solution of 0.75 g (0.005 mole) of 3,3-dimethylcysteine in 7.5 ml (0.007 mole) of N NaOH was added. The mixture was stirred vigorously for 15 minutes at −8°, and was then stirred for one hour at room temperature. The aqueous layer was separated, extracted with ether, and acidified to Congo red with 2 N HCl with cooling. The oil that came down slowly solidified. The product was 0.6 g (40%) of (N-formyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine, m.p. 152-161°, raised to 181-183° by repeated recrystallization from a methanol-ether mixture. The peptide is readily soluble in alcohol and dioxane; it is insoluble in ether, water, and benzene.

Found %: C 43.46; H 6.53; N 8.54; S 19.86

$C_{11}H_{20}O_4N_2S_2$. Calculated %: C 42.85; H 6.49; N 9.09; S 20.50

Methyl Ester of (N-Acetyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine. To a solution of 0.5 g (0.0028 mole) of N-acetyl-3,3-dimethylcysteine β-thiolactone [1] in ethyl acetate, 0.45 g (0.0028 mole) of the methyl ester of 3,3-dimethylcysteine was added. The reaction mixture was set aside at room temperature until the next day, when the precipitate formed was filtered off and washed with ethyl acetate. The product was 0.3 g of (N-acetyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine, m.p. 194-196° (from ethyl acetate). The ethyl acetate mother liquor was evaporated under reduced pressure, and the oily residue was washed with 2 N HCl and with water: a further 0.4 g of the dipeptide was obtained. The total yield was 0.7 g (73.7%). The methyl ester of (N-acetyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine is readily soluble in alcohol and ethyl acetate, but insoluble in water, ether, and benzene.

Found %: C 46.20; H 7.12; S 19.01; N 8.22

$C_{13}H_{24}O_4N_2S_2$. Calculated %: C 46.42; H 7.14; S 19.04; N 8.33

(N-Acetyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine. a) A mixture of 0.5 g (0.0015 mole) of the methyl ester of (N-acetyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine and 2 N NaOH was heated at 40° for two hours. The alkaline solution was extracted with ether and then acidified to Congo red with 2 N HCl The precipitate that formed was filtered off and washed with water. The product was 0.25 g (50%) of (N-acetyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine, melting with decomposition at 205-206° (from methanol). (N-acetyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine is an amorphous substance, readily soluble in alcohol and dioxane, insoluble in water, ether, and benzene. The presence of a thiol group in the dipeptide can be detected by the usual reactions.

Found %: C 44.66; H 7.00; S 19.80; N 8.57

$C_{12}H_{24}O_4N_2S_2$. Calculated %: C 44.72; H 6.83; S 19.86; N 8.72

Neutralization equivalent: found 316.4; calculated 322

b) A solution of 1.2 g (0.006 mole) of N-acetyl-3,3-dimethylcysteine and 1.2 g (0.012 mole) of triethylamine in 20 ml of dry chloroform was cooled to −10° and stirred while addition was made of a cooled solution of 0.8 g (0.006 mole) of isobutyl chloroformate in dry chloroform. The reaction mixture was allowed to stand at −6° until there was no longer a reaction for thiol with ferric chloride. After 5-10 minutes the solution was cooled to −10° and a cooled solution of 0.9 g (0.006 mole) of 3,3-dimethylcysteine in 6 ml of N NaOH (0.006 mole) was added. The mixture was stirred vigorously at 0° for 15 minutes, and was then stirred for one hour at room temperature. The aqueous layer was separated, extracted with ether, cooled, and acidified to Congo red with 2 N HCl. The oil that came down rapidly solidified. It was filtered off and washed with hot water and then methanol. The product was 1.2 g (60%) of (N-acetyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine, melting with decomposition at 205-206°. In admixture with the sample prepared in the preceding experiment there was no depression of melting point.

c) To a solution of 0.35 g (0.002 mole) of 3,3-dimethylcysteine in aqueous sodium bicarbonate (0.002 mole), 0.4 g (0.002 mole) of N-acetyl-3,3-dimethylcysteine β-thiolactone [1] was added. The mixture was heated at 30° until the thiolactone dissolved and was then left overnight at room temperature. The solution was then extracted several times with ethyl acetate and acidified to Congo red with 25% sulfuric acid; the oil that came down slowly solidified. The precipitate was filtered off, washed with water, and dried over phosphoric oxide in a vacuum desiccator. The product was 0.5 g (91% on the amount of thiolactone that reacted) of (N-acetyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine, m.p. 205-206°, undepressed by admixture of samples of the dipeptides obtained in the preceding experiments. Evaporation of the ethyl acetate mother liquors resulted in the recovery of 0.1 g of unchanged N-acetyl-3,3-dimethylcysteine β-thiolactone.

Methyl Ester of (3,3-Dimethyl-N-phenylacetylcysteinyl)-3,3-dimethylcysteine. A solution of 0.6 g (0.0024 mole) of 3,3-dimethyl-N-phenylacetylcysteine β-thiolactone and 0.4 g (0.0024 mole) of the methyl ester of 3,3-dimethylcysteine was prepared in ethyl acetate and was then left at room temperature overnight. The crystalline precipitate that formed was filtered off, washed with ethyl acetate, and dried. The product was 0.55 g of the methyl ester of (3,3-dimethyl-N-phenylacetylcysteinyl)-3,3-dimethylcysteine. The ethyl acetate mother liquor yielded a further 0.25 g of the dipeptide, the total yield being 80%. After recrystallization from absolute ethanol the melting point was 155-161°. The dipeptide is a colorless crystalline substance, readily soluble in alcohol and ethyl acetate, but insoluble in water and ether. The presence of a thiol group can be detected with iodine.

Found %: C 55.30; H 6.90; S 15.68; N 6.92

$C_{19}H_{28}O_4N_2S_2$. Calculated %: C 55.33; H 6.79; S 15.53; N 6.79

(3,3-Dimethyl-N-phenylacetylcysteinyl)-3,3-dimethylcysteine. The methyl ester of (3,3-dimethyl-N-phenylacetylcysteinyl)-3,3-dimethylcysteine (0.4 g, 0.001 mole) was heated with 2 N NaOH at 40-50° for two hours. The solution was filtered, extracted with ether, cooled, and acidified with 25% sulfuric acid. The oil that separated rapidly solidified. The precipitate was filtered off, washed with water, and dried over phosphoric oxide in a vacuum desiccator; it was then again washed with ether and dried. The product was 0.3 g (77%) of (3,3-dimethyl-N-phenylacetylcysteinyl)-3,3-dimethylcysteine, melting with decomposition at 178-182° (from absolute alcohol).

(3,3-Dimethyl-N-phenylacetylcysteinyl)-3,3-dimethylcysteine is readily soluble in alcohol, chloroform, and dioxane, but insoluble in water and ether. The presence of the thiol group can be detected both with iodine and with ferric chloride.

Found %: C 54.08; H 6.93; S 15.23; N 6.78

$C_{18}H_{26}O_4N_2S_2$. Calculated %: C 54.27; H 6.53; S 16.03; N 7.03

Bis(3,3-Dimethyl-N-phenylacetylcysteinyl)cystine. To a solution of 0.12 g (0.0005 mole) of cystine in 1 ml of N NaOH (0.001 mole), 0.25 g (0.001 mole) of 3,3-dimethyl-N-phenylacetylcysteine β-thiolactone was added. The mixture was heated to 50° and then left at room temperature overnight. On the next day the solution was extracted with ethyl acetate and acidified to Congo red with 2 N HCl with cooling. The amorphous precipitate that formed was filtered off, washed with water, and dried over phosphoric oxide in a vacuum desiccator. The product was 0.35 g of bis(3,3-dimethyl-N-phenylacetylcysteinyl)cystine, which had a decomposition temperature of 96°. The substance was purified by precipitation from methanol solution with absolute ether (repeated twice), and it then melted with decomposition at 160°. The dipeptide is readily soluble in alcohol, but insoluble in water, ether, and benzene. The presence of the thiol group could be detected only by the iodine reaction.

Found %: S 16.15; N 7.39

$C_{32}H_{42}O_8N_4S_4$. Calculated % S 17.34; N 7.58

(3,3-Dimethyl-N-phenylacetylcysteinyl)valine. Valine (0.12 g, i.e. 0.001 mole) was dissolved in an aqueous solution of sodium bicarbonate (0.001 mole), and 0.25 g (0.001 mole) of 3,3-dimethyl-N-phenylacetylcysteine β-thiolactone was added. The mixture was heated in a water bath at 40-45° until the thiolactone dissolved (20 minutes), and was then left overnight. It was then filtered, and the filtrate was extracted with ethyl acetate and acidified to Congo red with sulfuric acid with cooling. The oil that separated solidified after some time. The product was 0.3 g of (3,3-dimethyl-N-phenylacetylcysteinyl)valine, decomposition temperature 159°, raised to 183° by two crystallizations from absolute ethanol. The dipeptide is readily soluble in alcohol, dioxane, ethyl acetate, and chloroform, but insoluble in water and ether. The presence of a thiol group can be detected only by the iodine reaction.

Found %: C 58.71; H 6.96; S 8.72; N 7.67

$C_{18}H_{26}O_4N_2S$. Calculated %: C 59.01; H 7.10; S 8.74; N 7.65

(N-Formyl-3,3-dimethylcysteinyl)alanine. To a solution of 0.18 g (0.002 mole) of alanine in 2 ml of N NaOH (0.002 mole), 0.32 g (0.002 mole) of N-formyl-3,3-dimethylcysteine β-thiolactone was added. The mixture was heated at 40° for 20 minutes and then set aside at room temperature overnight. The solution was extracted with ethyl acetate, acidified with 2 N HCl with cooling, and evaporated under reduced pressure until crystallization set in. The product was 0.35 g of (N-formyl-3,3-dimethylcysteinyl)alanine, decomposition temperature 163°. The mother liquor yielded a further 0.1 g of the dipeptide, the total yield being 0.45 g. After recrystallization from ethanol the decomposition temperature was 163°. The dipeptide is readily soluble in alcohol, dioxane, and water, but insoluble in ether, ethyl acetate and benzene. The presence of a thiol group can be detected by the iodine reaction.

Found %: C 43.94; H 6.49; S 13.28; N 10.90

$C_9H_{16}O_4N_2S$. Calculated %: C 43.58; H 6.45; S 12.90; N 11.29

[N-Acetyl-S-(isobutoxycarbonyl)-3,3-dimethylcysteinyl]-3,3-dimethylcysteine β-Thiolactone (I). A solution of 0.30 g (0.001 mole) of (N-acetyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine and 0.3 g (0.003 mole) of triethylamine in dry chloroform was cooled to −10°, and at this temperature a solution of 0.14 g (0.001 mole) of isobutyl chloroformate in dry chloroform was added. Five minutes after a ferric chloride reaction ceased to be obtained for the thiol group, the temperature was gradually raised to that of the room. Solvent was removed under reduced pressure. The oily residue was rubbed out with ether, and the precipitate then formed was filtered off, washed with water, and dried over phosphoric oxide in a vacuum desiccator. The product was 0.1 g of the thiolactone (I), m.p. 196-198° (from absolute alcohol). The thiolactone does not react with water at room temperature, but when heated with water it is readily hydrolyzed with formation of (N-acetyl-3,3-dimethylcysteinyl)-3,3-dimethylcysteine. It is readily soluble in alcohol, chloroform, and ethyl acetate, but insoluble in water and ether.

Found %: C 50.16; H 6.92; S 15.80; N 6.77

$C_{17}H_{28}O_5N_2S_2$. Calculated %: C 50.49; H 6.93; S 15.84; N 6.93

Anilide of [N-Acetyl-S-(isobutyoxycarbonyl)-3,3-dimethylcysteinyl]-3,3-dimethylcysteine. A solution of 0.1 g (0.0002 mole) of the thiolactone (I) and 0.04 g (0.0004 mole) of aniline was prepared in ethyl acetate as solvent and was set aside at room temperature overnight. The crystalline precipitate formed was then filtered off, washed with 2 N HCl and then water, and dried. The product was 0.1 g of the anilide of [N-acetyl-S-(isobutyoxycarbonyl)-3,3-dimethylcysteinyl]-3,3-dimethylcysteine, m.p. 226-229° (from absolute alcohol). The anilide is readily soluble in alcohol, but insoluble in water, ethyl acetate, and ether.

Found %: C 55.08; H 7.05; S 13.09; N 8.76

$C_{23}H_{25}O_5N_3S_2$. Calculated %: C 55.53; H 7.04; S 12.88; N 8.45

Methyl Ester of {[N-Acetyl-S-(isobutoxycarbonyl)-3,3-dimethylcysteinyl]-3,3-dimethylcysteinyl}-3,3-dimethylcysteine (II). A solution of 0.1 g (0.00025 mole) of [N-acetyl-S-(isobutoxycarbonyl)-3,3-dimethylcysteinyl]-3,3-dimethylcysteine β-thiolactone and 0.04 g (0.00025 mole) of the methyl ester of 3,3-dimethylcysteine was prepared in ethyl acetate as solvent and was set aside at room temperature overnight. The precipitate formed was filtered off, washed with ether, and dried. The product was 0.1 g of the methyl ester of {[N-acetyl-S-(isobutoxycarbonyl)-3,3-dimethylcysteinyl]-3,3-dimethylcysteinyl}-3,3-dimethylcysteine, melting with decomposition at 236-238° (from absolute alcohol). The dimethylcysteine tripeptide (II) is an amorphous substance, readily soluble in alcohol, but insoluble in water, ether, and ethyl acetate.

Found %: C 48.00; H 7.10; S 16.85; N 7.36

$C_{23}H_{41}O_7N_3S_3$. Calculated %: C 48.67; H 7.31; S 16.94; N 7.38

Methyl Ester of (3,3-Dimethyl-N-phenaceturylcysteinyl)-3,3-dimethylcysteine (IV). 3,3-Dimethyl-N-phenaceturylcysteine β-thiolactone (III) [1] (0.2 g, i.e. 0.00065 mole) and the methyl ester of 3,3-dimethylcysteine (0.1 g, i.e. 0.00065 mole) was heated with 20 ml of absolute methanol until a solution was obtained. The solution was set aside at room temperature overnight. Solvent was removed under reduced pressure, and the oily residue was rubbed out with ether. The precipitate formed was filtered off and washed with hot ethyl acetate. The product was 0.21 g of the methyl ester of (3,3-dimethyl-N-phenaceturylcysteinyl)-3,3-dimethylcysteine, m.p. 192-200°. The tripeptide (IV) is soluble in alcohol and ethyl acetate, but insoluble in water, ether, and chloroform. In this tripeptide the thiol group can be detected only by the iodine reaction.

Found %: C 53.33; H 6.47; S 13.15; N 8.29

$C_{21}H_{30}O_5N_3S_2$. Calculated %: C 53.84; H 6.41; S 13.67; N 8.91.

(3,3-Dimethyl-N-phenaceturylcysteinyl)-3,3-dimethylcysteine. a) Hydrolysis of (IV) with alcoholic NaOH. The methyl ester of (3,3-dimethyl-N-phenaceturylcysteinyl)-3,3-dimethylcysteine (0.25 g, i.e. 0.0005 mole) was dissolved in excess of alcoholic N NaOH, and the solution was set aside at room temperature overnight. Solvent was removed under reduced pressure, and the residue was dissolved in water. The solution was acidified to Congo red with 2 N HCl, and an oil formed, which solidified when the mixture was placed in a refrigerator. The precipitate was filtered off, washed with water, and dried over phosphoric oxide in a vacuum desiccator. The product was 0.15 g (68%) of (3,3-dimethyl-N-phenaceturylcysteinyl)-3,3-dimethylcysteine, melting with decomposition at 199-203° (from a mixture of ethyl acetate and methanol). (3,3-Dimethyl-N-phenaceturylcysteinyl)-3,3-dimethylcysteine is readily soluble in water and ether.

Found %: S 13.39; N 8.77

$C_{20}H_{29}O_5N_3S_2$. Calculated %: S 14.06; N 9.23

b) 3,3-Dimethyl-N-phenaceturylcysteine β-thiolactone (1 g, i.e. 0.003 mole) was added to a solution of 0.5 g (0.003 mole of 3,3-dimethylcysteine in aqueous sodium bicarbonate (0.003 mole). The mixture was heated at 30° until the thiolactone was dissolved, and was then set aside at room temperature overnight. On the next day the solution was extracted with ethyl acetate and acidified to Congo red with 25% sulfuric acid. When the mixture was cooled, the precipitated oil solidified. It was filtered off, washed with water, and dried over phosphoric oxide in a vacuum desiccator. The product was 0.9 g (60%) of (3,3-dimethyl-N-phenaceturylcysteinyl)-3,3-dimethylcysteine, m.p. 155-168°, raised by repeated recrystallizations from dioxane and alcohol to 199-203°. In admixture with the product of the preceding experiment there was no depression in melting point.

3-Methyl-2-(3-methyl-2-phenaceturamidocrotonamido)crotonic Acid (V). The methyl ester of (3,3-dimethyl-N-phenaceturylcysteinyl)-3,3-dimethylcysteine (0.46 g, i.e. 0.001 mole) was heated for two hours at 50-60° with 2 N NaOH. The solution was cooled, extracted with ether, and acidified to Congo red with 2 N HCl. The oily precipitate formed solidified after a time and was filtered off, washed with water, and dried over phosphoric oxide in a vacuum desiccator. The product was 0.25 g (65%) of 3-methyl-2-(3-methyl-2-phenaceturamidocrotonamido)crotonic acid, m.p. 193-196° (from ethanol). The acid (V) decolorizes a solution of bromine in chloroform, and it is readily soluble in alcohol and dioxane, poorly soluble in ethyl acetate and acetone, and insoluble in ether and water.

Found %: C 61.50; H 6.41; N 10.08

$C_{20}H_{25}O_5N_3$. Calculated %: C 62.00; H 6.45; N 10.85

(3,3-Dimethyl-N-phenaceturylcysteinyl)valine (VI). 3,3-Dimethyl-N-phenaceturylcysteine β-thiolactone (0.15 g) was dissolved in warm alcohol, an aqueous solution of the sodium salt prepared from 0.66 g of valine was added, and the mixture was heated to 50°. On the next day the mixture was evaporated under reduced pressure to one-third bulk and was then acidified to Congo red with 2 N HCl. The precipitate formed was filtered off, washed with water, and dried. The product was 0.15 g of (3,3-dimethyl-N-phenaceturylcysteinyl)valine, melting with decomposition at 178-184° (from absolute ethanol).

Found %: C 56.85; H 6.93; S 7.36; N 10.1

$C_{20}H_{29}O_5N_3S$. Calculated %: C 56.73; H 6.85; S 7.54; N 9.92

[S-(Isobutoxycarbonyl)-3,3-dimethyl-N-phenaceturylcysteinyl]-3,3-dimethylcysteine β-Thiolactone (VII). A solution of 0.2 g (0.0004 mole) of (3,3-dimethyl-N-phenaceturylcysteinyl)-3,3-dimethylcysteine and 0.13 g (0.0012 mole) of triethylamine in dry chloroform was cooled to −10°, and at this temperature a solution of 0.084 g (0.0006 mole) of isobutyl chloroformate in dry chloroform was added. Five minutes after the ferric chloride reaction for thiol ceased to be obtained, the temperature was brought to that of the room. Solvent was removed under reduced pressure, the residue was rubbed out with ether, and the precipitate was filtered off, washed with water, and dried over phosphoric oxide in a vacuum desiccator. The product was 0.14 g of the thiolactone (VII), m.p. 130-141°, raised to 164-166° (with decomposition) by recrystallization from aqueous acetone. The thiolactone gradually decolorized iodine. After hydrolysis with alcoholic caustic alkali at room temperature, a positive reaction for the thiol group was given.

Found %: C 55.01; H 6.67; S 11.48; N 7.86

$C_{25}H_{35}O_6N_3S_2$. Calculated %: C 55.86; H 6.70; S 11.91; N 7.82

Conversion of (3,3-Dimethyl-N-phenaceturylcysteinyl)valine into the Anhydride (VIII). A solution of 0.43 g (0.001 mole) of (3,3-dimethyl-N-phenaceturylcysteinyl)valine (VI) and 0.2 g (0.002 mole) of triethylamine in dry chloroform was cooled to −10°, and at this temperature a solution of 0.28 g (0.002 mole) of isobutyl chloroformate in dry chloroform was added. After 10 minutes the temperature was brought to that of the room. Solvent was removed under reduced pressure and the residue was rubbed out with ether. Triethylamine hydrochloride was filtered off. The product was 0.25 g of the substance (VIII), melting with decomposition at 155-158°. The substance (VIII) is readily soluble in alcohol and dioxane, poorly soluble in ether, and insoluble in water.

Found %: C 58.91; H 6.82; S 6.14; N 8.57

$C_{25}H_{36}O_6N_3S$. Calculated %: C 59.40; H 6.93; S 6.33; N 8.31

Methyl Ester of [S-(Isobutyoxycarbonyl)-3,3-dimethyl-N-phenaceturylcysteinyl]-valyl-3,3-dimethylcysteine (IX). A solution of 0.1 g (0.0002 mole) of the substance (VIII) and 0.04 g (0.00025 mole) of the methyl ester of 3,3-dimethylcysteine was prepared in ethyl acetate as solvent and was set aside at room temperature overnight. The solution was filtered, and was washed with 2 N HCl, with water, with sodium bicarbonate solution, and again with water. It was dried over magnesium sulfate, and solvent was removed under reduced pressure. The residue was reprecipitated three times from ethyl acetate solution by means of ether; it then melted with decomposition at 145-178°. The tetrapeptide (IX) is an amorphous substance, and could not be crystallized. The presence of the thiol group can be detected only by the iodine reaction; with ferric chloride the reaction is negative.

Found %: C 56.19; H 7.06; N 7.84

$C_{31}H_{48}O_8N_4S_2$. Calculated %: C 55.68; H 7.18; N 8.38

SUMMARY

1. It was shown that N-acyl-3,3-dimethylcysteine β-thiolactones are active acylating agents, similar in properties to mixed anhydrides. By the acylation of amino acids with these β-thiolactones, various polyamides can be prepared, and these include compounds containing residues of mercapto amino acids. A fundamentally new method for the synthesis of polypeptides has therefore been provided.

2. By the aid of the new method, di- and tri-peptides were prepared, and these include both polypeptides derived entirely from mercapto amino acids and also mixed polypeptides.

LITERATURE CITED

[1] I. Knunyants, O. Kildisheva, and E. Pervova, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. 1955, No. 4, 689. (T. p. 613)*.

Received October 15, 1954

N. D. Zelinsky Institute of Organic
Chemistry of the U.S.S.R. Academy of Sciences

---

* T. p. = C. B. Translation pagination

BLANK
PAGE

ADDITION REACTIONS OF PERFLUOROOLEFINS

COMMUNICATION 3. ADDITION OF SULFUR CHLORIDES

I. L. Knunyants and A. V. Fokin

It has been shown in previous communications [1, 2] that perfluoroolefins are peculiar chemically in their ability to undergo ready addition with nucleophilic reagents (alkoxides, thiols, amines, etc.). It was then suggested that the primary process determining addition to perfluoroolefins is the anionoid attack of the nucleophilic reagent resulting from electron deficiency in the π-bond of the perfluoroolefin. The π-bond of the tetrafluoroethylene molecule plays the part of an electron-acceptor in reactions with nucleophilic reagents, whereas in the usual olefins it acts as an electron-donor. The peculiar structure of the π-bond of perfluoroolefins explains also the difficulty with which electrophilic reagents add to them.

After many unsuccessful attempts, in 1950 we succeeded in bringing about the addition of sulfur chlorides to tetrafluoroethylene. It was found that this reaction, unlike that of the usual olefins with sulfur chlorides (which go readily in the cold), takes place only at high temperature and under pressure. When tetrafluoroethylene was heated with sulfur monochloride at 80-90° for 6-8 hours, only a low yield (not more than 18-20%) of addition products was obtained. Only when the mixture was heated at 100-120° for six hours was it found possible to attain a yield of about 80%. The product of the reaction of tetrafluoroethylene with sulfur monochloride was a complex mixture, consisting of mono-, di-, tri-, and poly-sulfides and various sulfenyl chlorides. By fractionation the following previously unknown compounds were isolated: 2-chloro-1,1,2,2-tetrafluoroethanesulfenyl chloride (I), bis(2-chloro-1,1,2,2-tetrafluoroethyl) sulfide (IV), bis(2-chloro-1,1,2,2-tetrafluoroethyl)disulfide (V), and higher polysulfides (see table).

The main reaction product was bis(2-chloro-1,1,2,2-tetrafluoroethyl) disulfide. Purification of this disulfide presented much difficulty, and even after many distillations it could not be freed from material containing active chlorine. When the crude disulfide was boiled with cyclohexene, subsequent fractional distillation yielded the disulfide in a pure state, and it was shown that the impurity originally present in the disulfide was 1-chloro-2-(chlorodithio)-1,1,2,2,-tetrafluoroethane (II), which reacts with cyclohexene with formation of the high-boiling 2-chlorocyclohexyl 2-chloro-1,1,2,2-tetrafluoroethyl disulfide (IX), readily separable from bis(2-chloro-1,1,2,2-tetrafluoroethyl) disulfide by distillation. The latter compound, therefore, was obtained in the pure state. The structure of bis(2-chloro-1,1,2,2-tetrafluoroethyl)disulfide was proved by the chlorine cleavage reaction. This reaction, which proceeds with most aliphatic disulfides with evolution of heat, was here found to require unexpectedly severe conditions. Negative results were obtained when dry chlorine was passed for two hours at room temperature and when treatments were given in a sealed tube with sulfuryl chloride at 120-140° and with bromine at 120°. It was found possible to effect the cleavage of the disulfide in quantitative yield by the action of chlorine at 80-90° (in an autoclave):

$$ClCF_2CF_2S-SCF_2CF_2Cl + Cl_2 \longrightarrow 2ClCF_2CF_2SCl.$$

The reaction product was a clear, mobile liquid, b.p. 69.5°. Analysis for active chlorine, fluorine, and sulfur showed that the compound was 2-chloro-1,1,2,2-tetrafluoroethanesulfenyl chloride. It liberated iodine from potassium iodide solution, and by treatment of an ethereal solution of the sulfenyl chloride with potassium iodide solution, a satisfactory yield of the original bis(2-chloro-1,1,2,2-tetrafluoroethyl) disulfide was obtained:

$$2ClCF_2CF_2SCl + 2HI \longrightarrow ClCF_2CF_2S-SCF_2CF_2Cl + I_2 + 2HCl.$$

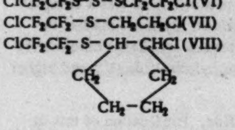
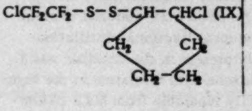
2-Chloro-1,1,2,2-tetrafluoroethanesulfenyl chloride reacted smoothly with diethylamine with formation of N,N-diethyl-2-chloro-1,1,2,2-tetrafluoroethanesulfenamide (III):

$$ClCF_2CF_2S-Cl + 2NH(C_2H_5)_2 \longrightarrow ClCF_2CF_2S-N(C_2H_5)_2 + HCl NH(C_2H_5)_2.$$

It was found, however, that 2-chloro-1,1,2,2-tetrafluoroethanesulfenyl chloride is less reactive toward olefins than its hydrogen analog. At ordinary temperatures it adds neither to ethylene nor to cyclohexene. The sulfides formed with ethylene and with cyclohexene were obtained only when the reactants were heated in a sealed glass tube. The products were 2-chloroethyl 2-chloro-1,1,2,2-tetrafluoroethyl sulfide (VII) and 2-chlorocyclohexyl 2-chloro-1,1,2,2-tetrafluoroethyl sulfide (VIII).

The addition of sulfur dichloride to tetrafluoroethylene was carried out at 100-110°, and the yield of addition products attained 80%. The products were the same as those of the reaction with sulfur monosulfide. The chlorine formed by the dissociation of sulfur dichloride reacted with tetrafluoroethylene and with the addition products, and the reaction mixture was enriched in sulfenyl chlorides formed by the cleavage of di- and poly-sulfides. The amount of disulfide was therefore correspondingly reduced, and it was found to be possible to isolate 2-chloro-1,1,2,2-tetrafluoroethanesulfenyl chloride and 1-chloro-2-(chlorodithio)-1,1,2,2-tetrafluoroethane in appreciable amounts. When the chlorodithio compound, which was isolated in the pure state, was heated with cyclohexene, it was converted in good yield into 2-chlorocyclohexyl 2-chloro-1,1,2,2-tetrafluoroethyl disulfide, which was isolated previously from the products of the treatment of a reaction mixture with cyclohexene. The di- and tri-sulfides obtained were found to be stable substances.

TABLE

Formula	B.p. in °C (p in mm)	Sp. gr. at 20°	Refractive index at 20°
$ClCF_2CF_2SCl$ (I)	69.5°	1.605	1.3890
$ClCF_2CF_2S-SCl$ (II)	126	1.674	1.4112
$ClCF_2CF_2S-N(C_2H_5)_2$ (III)	66-67 (60)	1.341	1.4850
$ClCF_2CF_2SCF_2CF_2Cl$ (IV)	100-102	1.662/10°	1.368/10°
$ClCF_2CF_2S-SCF_2CF_2Cl$ (V)	139-140	1.685	1.3970
$ClCF_2CF_2S-S-SCF_2CF_2Cl$ (VI)	50-52 (5)	1.707	1.4340
$ClCF_2CF_2-S-CH_2CH_2Cl$ (VII)	85 (100)	1.528	1.4218
 (VIII)	135-136 (60)	1.388	1.4595
 (IX)	142 (20)	1.456	1.4915

EXPERIMENTAL

1. Products of the Addition of Sulfur Monochloride to Tetrafluoroethylene. A mixture of 13.5 g of freshly distilled sulfur monochloride and 25 g of liquid tetrafluoroethylene was prepared in a stainless steel cylinder, which was hermetically sealed and then heated with constant agitation at 100-120° for six hours. Unchanged tetrafluoroethylene (1.5 liters) was driven off, and 28 g of addition products was obtained. The reaction mixture – a clear, light-yellow liquid – was fractionated at ordinary pressure, and yielded:

Fraction I, b.p. 68-74°, 2.8 g
Fraction II, b.p. 95-105°, 3.5 g
Fraction III, b.p. 130-142°, 1.4 g

The residue was fractionated at reduced pressure and yielded:

Fraction IV, b.p. 50-52° (5 mm); 3 g
Fraction V, b.p. 96-98° (5 mm); 2 g

Redistillation of Fraction I yielded about 2 g of a substance boiling at 69-70°. This was 2-chloro-1,1,2,2-tetrafluoroethanesulfenyl chloride and had d_4^{20} 1.604; n_D^{20} 1.3893; found MR 29.93; calculated MR 29.49.

Found %: S 15.44; F 34.22
$C_2SF_4Cl_2$. Calculated %: S 15.80; F 34.70

Fraction II yielded a substance boiling at 100-102°. This was bis(2-chloro-1,1,2,2-tetrafluoroethyl) sulfide; d_4^{10} 1.662; n_D^{10} 1.368; found MR 40.06; calculated MR 39.16.

Found %: S 11.02; Cl 22.75; F 47.55
$C_4F_8Cl_2S$. Calculated %: S 11.50; Cl 23.40; F 49.90

Fraction III was purified by heating it with cyclohexene and then distilling at ordinary pressure, when bis(2-chloro-1,1,2,2-tetrafluoroethyl) disulfide was isolated in 35% yield (11.7 g). It is a colorless, mobile liquid, b.p. 139-140°; d_4^{20} 1.685; n_D^{20} 1.3970; found MR 47.60; calculated MR 46.85.

Found %: S 18.72; F 45.37; Cl 21.17
$C_4S_2F_8Cl_2$. Calculated %: S 19.10; F 45.45; Cl 21.22
Found M 332.6 (cryoscopically)
Calculated M 335

Vacuum distillation of Fraction IV yielded bis(2-chloro-1,1,2,2-tetrafluoroethyl) trisulfide, a colorless oily liquid, b.p. 50–52° (5mm); d_4^{20} 1.707; n_D^{20} 1.4340; found MR 55.60; calculated MR 54.52.

%: S 25.84; Cl 19.94; F 41.42

$C_4S_3F_8Cl_2$. Calculated %: S 26.16; Cl 19.34; F 41.25

The fractions of still higher boiling point were not investigated.

2. 2-Chloro-1,1,2,2-tetrafluoroethanesulfenyl Chloride. A mixture of 12 g of bis(2-chloro-1,1,2,2-tetrafluoroethyl) disulfide and 5 g of dry liquid chlorine was prepared in a stainless steel cylinder, which was hermetically sealed and heated with agitation at 95-100° for two hours. The residue after removal of excess of chlorine was 15 g of a light-yellow liquid, which had the characteristic odor of sulfenyl chlorides. Fractionation yielded 13 g of a substance boiling at 69.5°. This was 2-chloro-1,1,2,2-tetrafluoroethanesulfenyl chloride, obtained in 89% yield. It is a light-yellow mobile liquid, for which d_4^{20} 1.605; n_D^{20} 1.3890; found MR 30.04; calculated MR 29.49.

Found %: S 15.82; Cl 34.80; F 37.11

$C_2SF_4Cl_2$. Calculated %: S 15.80; Cl 34.70; F 37.42

3. 2-Chloroethyl 2-Chloro-1,1,2,2-tetrafluoroethyl Sulfide. A solution of 25 g of 2-chloro-1,1,2,2-tetrafluoroethanesulfenyl chloride in 40 g of carbon tetrachloride was introduced into a 250-ml stainless steel autoclave, which was then filled with ethylene from a cylinder until the pressure attained 35 atm. The autoclave was heated with continuous rotation for three hours at 95-100°, and the pressure in the autoclave fell to 19 atm. Excess of ethylene was removed from the reaction mixture, and the solvent was distilled off. The liquid residue (9 g) was vacuum-fractionated, and it yielded a main fraction boiling at 82-86° (100 mm). Redistillation yielded pure 2-chloroethyl-2-chloro-1,1,2,2-tetrafluoroethyl sulfide, a clear colorless oil liquid of characteristic odor and having b. p. 85° (100 mm); d_4^{20} 1.528; n_D^{20} 1.4218; found MR 38.39; calculated MR 38.72.

Found %: S 13.14; Cl 29.35; F 32.32

$C_4H_4F_7Cl_2S$. Calculated %: S 13.85; Cl 30.73; F 32.90

4. 2-Chlorocyclohexyl 2-Chloro-1,1,2,2-tetrafluoroethyl Sulfide. A mixture of 3 g of 2-chloro-1,1,2,2-tetrafluoroethanesulfenyl chloride and 4 g of cyclohexene was sealed in a tube, which was then heated in a water bath for one hour at 60-80°. Excess of cyclohexene was distilled off, and the residue (about 4.5 g) was vacuum-fractionated. The main fraction was collected at 135-136° (60 mm). Redistillation under vacuum yielded pure 2-chlorocyclohexyl 2-chloro-1,1,2,2-tetrafluoroethyl sulfide, a clear colorless oily liquid having b.p. 135° (60 mm); d_4^{20} 1.388; n_D^{20} 1.4595; found MR 56.15; calculated MR 55.00.

Found %: S 11.55; Cl 24.52; F 28.15

$C_8H_{10}F_4SCl_2$. Calculated %: S 11.23; Cl 24.91; F 26.66

5. 2-Chlorocyclohexyl 2-Chloro-1,1,2,2-tetrafluoroethyl Disulfide. The residue that remained after the distillation at ordinary pressure of the oil obtained by the treatment of crude bis(2-chloro-1,1,2,2-tetrafluoroethyl) disulfide with cyclohexene (Experiment 1) was vacuum-distilled and yielded a substance boiling at 142° (20 mm). This was 2-chlorocyclohexyl 2-chloro-1,1,2,2-tetrafluoroethyl disulfide, having d_4^{20} 1.456 and n_D^{20} 1.4915.

Found %: S 20.04; Cl 21.25; F 24.53

$C_8H_{10}F_4Cl_2$. Calculated %: S 29.40; Cl 22.40; F 23.96

A mixture of this disulfide (4.6 g) and dry liquid chlorine (3 g) was prepared in a 30-ml steel cylinder, which was hermetically sealed and heated at 100° for two hours. The residue remaining after removal of excess of chlorine was about 6 g of a liquid having an odor of sulfenyl chlorides. Fractionation yielded 3 g of a substance boiling at 69-70°. It was a clear mobile light-yellow liquid having d_4^{20} 1.605 and n_D^{20} 1.3899 (2-chloro-1,1,2,2-tetrafluoroethanesulfenyl chloride).

Found %: S 15.38; Cl 34.33; F 36.85

$C_2SF_4Cl_2$. Calculated %: S 15.80; Cl 34.70; F 37.42

6. Products of the Addition of Sulfur Dichloride to Tetrafluoroethylene. A mixture of 10.3 g of freshly prepared sulfur dichloride and 24 g of liquid tetrafluoroethylene was prepared in a 100-ml stainless steel cylinder, which was hermetically sealed and heated at 100-110° for five hours. The cylinder was cooled, and the excess of tetrafluoroethylene was driven off (0.8 liter). The weight of the liquid residue was 25.5 g. Fractionation yielded:

Fraction I B.p. 66-72°; 6 g
Fraction II B.p. 120-128°; 8.5 g
Fraction III B.p. 126-142°; 3 g

The residue remaining undistilled at ordinary pressure was 4.5 g.

Redistillation of Fraction I yielded 2-chloro-1,1,2,2-tetrafluoroethanesulfenyl chloride, b.p. 69-70°; d_4^{20} 1.681; n_D^{20} 1.3955.

Fraction II yielded 1-chloro-2-(chlorodithio)-1,1,2,2-tetrafluoroethane, a mobile orange liquid having b.p. 126°; d_4^{20} 1.674; n_D^{20} 1.4112.

Found %: S 27.38; Cl 30.82; F 33.11
$C_2F_4Cl_2S_2$. Calculated %: S 27.20; Cl 30.25; F 32.35

7. Addition of Cyclohexene to 1-Chloro-2-(chlorodithio)-1,1,2,2-tetrafluoroethane. A mixture of 8 g of 1-chloro-2-(chlorodithio)-1,1,2,2-tetrafluoroethane and 4 g of cyclohexene was sealed in a glass tube, which was then heated at 60° for two hours. Fractionation of the reaction mixture yielded a substance having b.p. 136-137° (18 mm), d_4^{20} 1.458, and n_D^{20} 1.4912 (2-chlorocyclohexyl 2-chloro-1,1,2,2-tetrafluoroethyl disulfide).

Found %: S 20.83; Cl 20.10; F 23.22
$C_8H_{10}S_2F_4Cl_2$. Calculated %: S 20.19; Cl 22.40; F 23.96

8. Bis(2-chloro-1,1,2,2-tetrafluoroethyl) Disulfide. A solution of 12 g of 2-chloro-1,1,2,2-tetrafluoroethanesulfenyl chloride in 100 ml of ether was introduced into a 250-ml separating funnel, and 10% potassium iodide solution was added gradually, the reaction mixture being carefully shaken after each addition. The ether layer was separated, washed with thiosulfate solution, and dried with calcined magnesium sulfate. After removal of ether, the residue was fractionated at ordinary pressure. The main fraction boiled at 133-144°. Redistillation yielded a substance boiling at 140-141° (4.5 g), which corresponded in physical properties to bis(2-chloro-1,1,2,2-tetrafluoroethyl) disulfide. It had d_4^{20} 1.685 and n_D^{20} 1.3965.

Found %: S 19.87
$C_4F_8Cl_2S_2$. Calculated %: S 19.10

9. N,N-Diethyl-2-chloro-1,1,2,2-tetrafluorethanesulfenamide. A solution of 8 g of 2-chloro-1,1,2,2-tetrafluoroethanesulfenyl chloride in 50 ml of dry ether was introduced into a 100-ml round-bottomed flask fitted with a stirrer. The solution was constantly stirred and cooled while a solution of 4 g of diethylamine in dry ether was added in small portions. Reaction was accompanied by the evolution of much heat. The solution was separated from the precipitate of diethylamine hydrochloride, and ether was then distilled off. Vacuum fractionation yielded a main fraction boiling at 64-69° (60 mm), and redistillation gave pure N,N-diethyl-2-chloro-1,1,2,2-tetrafluoroethanesulfenamide, b.p. 66-67° (60 mm), d_4^{20} 1.341 and n_D^{20} 1.4850.

Found %: S 12.94; N 6.21; F 32.54
$C_6H_{10}F_4ClSN$. Calculated %: S 13.20; N 5.86; F 31.75

SUMMARY

1. Reaction of sulfur chlorides with tetrafluoroethylene yielded bis(2-chloro-1,1,2,2-tetrafluoroethyl) disulfide, 2-chloro-1,1,2,2-tetrafluoroethanesulfenyl chloride, and 1-chloro-2-(chlorodithio)-1,1,2,2-tetrafluoroethane. When treated with chlorine, bis(2-chloro-1,1,2,2-tetrafluoroethyl) disulfide was converted into 2-chloro-1,1,2,2-tetrafluoroethanesulfenyl chloride.

2. Unlike its hydrogen analog, 2-chloro-1,1,2,2-tetrafluoroethanesulfenyl chloride adds to olefins only under severe conditions. By the reaction of this sulfenyl chloride with ethylene and with cyclohexene, the corresponding sulfides were prepared.

Received May 20, 1954

LITERATURE CITED

[1] I. L. Knunyants and A. V. Fokin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, No. 2, 261, (T.p. 279)*.

[2] I. L. Knunyants, A. I. Shchekotikhin, and A. V. Fokin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, No. 2, 282, (T.p. 255)*.

---

* T.p. = C. B. Translation pagination.

BLANK
PAGE

DEARYLATION OF Ar_2PbX_2 AS A METHOD OF SYNTHESIZING A NEW CLASS OF COMPOUNDS $ArPbX_3$.

K. A. Kocheshkov and E. M. Panov

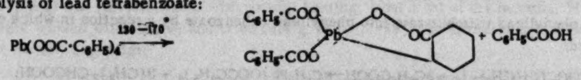
Of the existing three classes of organolead compounds R_3PbX, R_2PbX_2, and $RPbX_3$ (X is an acid residue and R an aliphatic or aromatic radical) the first two have been studied for a long time. Prior to our investigations [1, 2] no compounds of the last type containing aromatic radicals were known, and although compounds of formula $RPbX_3$ containing aliphatic radicals have been described, the available data on these is, for various reasons (see below), in need of verification.

In approaching the problem of synthesizing $ArPbX_3$ we may make use of analogies to other organometallic compounds of Group IV of the periodic system, taking into account, however, the peculiarities of lead. For example, the action of unstable lead tetrachloride on a diarylmercury would actually amount to the action of free chlorine, and not to an arylation reaction as in the case of germanium tetrachloride. When, however, in the reaction with diphenylmercury the lead tetrachloride is replaced by the fairly stable tetraacetate, the introduction of two aromatic radicals occurs:

$$2(C_6H_5)_2Hg + Pb(OOC\text{-}CH_3)_4 \longrightarrow (C_6H_5)_2Pb(OOCCH_3)_2 + 2C_6H_5HgOOCCH_3.$$

By this method Kocheshkov and Nad [3] prepared organolead compounds of the class Ar_2PbX_2 (X is the residue of an organic acid) having substituents in the aromatic nucleus, but they did not observe the formation of $ArPb(OOCCH_3)_3$.

Austin [4], following analogies from organomercury chemisty, attempted unsuccessfully to prepare $ArPbX_3$ by the pyrolysis of lead tetrabenzoate:



Methods based on disproportionation reactions in reverse have been applied successfully to aromatic tin compounds. It was by such a method that Kocheshkov [5] prepared members of the simplest class of organotin compounds $ArSnX_3$ for the first time. However, the application of this method in organolead chemistry does not result in the synthesis of $ArPbX_3$. When diphenyllead diisobutyrate is treated with lead tetraisobutyrate, the latter is reduced to lead diisobutyrate.

Again, according to Meyer [6], compounds of the type $RSnX_3$ can be prepared by the reaction

$$SnO_2HK + CH_3I \rightarrow CH_3SnOOH + KI$$

and Druce [7], following this analogy, attempted to prepare compounds of the type $RPbX_3$, but the process went in a different fashion:

$$2KI + PbO_2KH + H_2O \rightarrow 3KOH + PbI_2.$$

Lesbre [8], unlike Druce, found that Meyer's reaction could be applied to lead compounds and that in this way aliphatic compounds of the type $RPbX_3$ (X is a halogen) could be prepared.

However, in 1948 Calingaert and coworkers [9] repeated Lesbre's experiments and were unable to reproduce his results. It is doubtful whether the use by Lesbre of boiling concentrated hydrochloric acid in the synthesis would allow the compound $RPbX_3$ to remain undecomposed; it has been pointed out by several authors [10, 11] that such compounds are probably unstable to mineral acids. It is remarkable also that the compounds described by Lesbre were yellow, whereas all the compounds of the class $ArPb(OOC\text{-}R)_3$ that we have prepared are quite colorless (which is fully in accord with the well known lack of color in organic derivatives of quadrivalent lead).

Hence, after a critical examination of the data cited above, we considered it desirable to apply the reaction of dearylation with the aid of metal salts. In 1934, in a study of the action of mercuric chloride on various organometallic compounds, including Ar_4Pb, we noted that the reaction is arrested at the stage of elimination of two aromatic radicals. "There are no signs that the reaction can be arrested at the stage of formation of $C_6H_5PbCl_3$" [12]. This behavior was determined by the fact that the starting substance was diphenyllead dichloride, which is almost insoluble in organic solvents, and also by the fact that we were attempting to obtain $ArPbX_3$ compounds that were genetically associated with unstable lead tetrachloride. It was therefore necessary to replace halogen by an organic acid residue and, as experiment showed, to use mild conditions (room temperature; all of the starting substances in solution).

It was indeed found that, when a solution of a bivalent mercury salt in an organic acid was added to an organolead compound, also dissolved in an organic acid, the smooth elimination of one, two, three, or four radicals occurs, the number depending on the number of molecular proportions of mercury salt taken:

a) $(C_6H_5)_4Pb + Hg(OOCR)_2 \rightarrow (C_6H_5)_3PbOOCR + C_6H_5HgOOCR;$

b) $(C_6H_5)_3PbOOCR + Hg(OOCR)_2 \rightarrow (C_6H_5)_2Pb(OOCR)_2 + C_6H_5HgOOCR;$

c) $(C_6H_5)_2Pb(OOCR)_2 + Hg(OOCR)_2 \rightarrow C_6H_5 \cdot Pb(OOCR)_3 + C_6H_5HgOOCR;$

d) $C_6H_5Pb(OOCR)_3 + Hg(OOCR)_2 \rightarrow Pb(OOCR)_4 + C_6H_5HgOOCR.$

Our main concern was with the reaction of Equation (c) (the products obtained in (a) and (b) could be obtained in other ways).

It was shown by agreeing duplicate analyses that the products were pure and corresponded in composition to ArPbX3. This structure was further confirmed by

a) determining the number of acid groups (three):

$$C_6H_5Pb(OOCR)_3 + 3KOH \rightarrow C_6H_5PbOOH + 3RCOOK + H_2O;$$

b) eliminating the last (fourth) phenyl group by treatment with one molecular proportion of mercury salt, which resulted in the formation of crystalline lead tetraisobutyrate:

$$C_6H_5Pb[OOC \cdot CH(CH_3)_2]_3 + Hg[OOCCH(CH_3)_2]_2 \rightarrow Pb[OOCCH(CH_3)_2]_4 + C_6H_5HgOOCCH(CH_3)_2;$$

c) converting phenyllead triisobutyrate into phenyllead tribenzoate by a reaction in which exchange of acid residues occurred:

$$C_6H_5Pb[OOCCH(CH_3)_2]_3 + 3C_6H_5COOH \rightarrow C_6H_5Pb(OOCC_6H_5)_3 + 3(CH_3)_2CHCOOH;$$

d) converting phenyllead triisobutyrate by hydrolysis into benzeneplumbonic acid, and hence into phenyllead triacetate:

$$C_6H_5Pb[OOCCH(CH_3)_2]_3 \xrightarrow[H_2O]{NH_4OH} C_6H_5PbOOH \xrightarrow{3CH_3COOH} C_6H_5Pb(OOCCH_3)_3.$$

EXPERIMENTAL

Phenyllead Triacitate

Mercuric acetate (1.92 g = one molecular proportion) was warmed with 40 ml of glacial acetic acid, and the resulting solution was cooled to room temperature. Diphenyllead diacetate [3] (2.88 g = one molecular proportion) was then added; it rapidly went into solution. As reaction proceeded the amount of mercuric acetate present diminished, the change being followed by the following well known qualitative reaction: a drop of the solution was applied to a polished copper plate, and after a few seconds a dark spot appeared which became lighter when rubbed; from the intensity of the spot it was possible to get a rough idea of the concentration of unchanged mercury salt. After one day, when reaction was almost complete, 1.28 ml of alcoholic 4.7 N HCl (one molecular proportion) was added dropwise from a microburet in order to convert the phenylmercury acetate formed into phenylmercury chloride. The precipitate was filtered off and washed with alcohol. Its melting point was 253°, raised by crystallization from xylene to 258°, which corresponds to phenylmercury chloride; the yield was 1.6 g (80%). The filtrate was left in a vacuum desiccator over caustic potash until the acetic acid had evaporated away. The solid residue (3.63 g) was dissolved in 15 ml of hot dry freshly distilled ethyl acetate, and the solution was filtered. The filtrate was cooled in a mixture of salt and ice, and the crystals that separated were filtered off under suction and washed with hexane. The yield of phenyllead triacetate, m.p. 101-102°, was 2.19 g (79%).

The product (1 g) was recrystallized from 6 ml of hot ethyl acetate and the crystals were washed with hexane and with ether, vacuum-dried for five minutes at 61° (jacket of chloroform vapor), and then exposed to a vacuum for a further 30 minutes at room temperature. They were then ground in a mortar and again subjected to the same drying procedure. The melting point of the product (0.5 g) was unchanged at 101-102°.

Found %: Pb 45.93; 45.17

$C_{12}H_{14}O_6Pb$. Calculated %: Pb 44.92

Determination of the Number of Acetate Groups. A weighed amount (0.0649 g) of the substance was dissolved in alcohol and an excess of 0.1 N NaOH was added. Water was then added, and the excess of caustic soda was determined by titration with 0.1 N H_2SO_4. The volume of the caustic soda consumed in reaction with organolead compounds was found to be 4.45 ml (each acetate group corresponded to 1.41 ml of 0.1 N NaOH, and three acetate groups corresponded to 4.23 ml).

Phenyllead triacetate forms a loose mass of white needles resembling cotton wool. It is readily soluble in the cold in methanol, ethanol, chloroform, and acetic acid; it is moderately soluble in the cold in ethyl acetate and benzene, but dissolves readily when warmed with these solvents; it is of poor solubility in ether, and it does not dissolve in hexane even when heated.

Phenyllead Triisobutyrate

I. Yellow mercury oxide (2.16 g = one molecular proportion) was warmed with 9 ml of isobutyric acid, and the warm solution formed was cleared from slight turbidity by filtration. The filtrate was warmed with 5.32 g (one molecular proportion) of diphenyllead diisobutyrate [1], and the resulting solution was left in a dish over caustic alkali in a vacuum desiccator. After five days the precipitated crystals were filtered off and washed with cold hexane. The substance was dried in a vacuum for five minutes at 61° (jacket of chloroform vapor), and then exposed to a vacuum for not less than 30 minutes at room temperature. The yield of phenyllead triisobutyrate, m.p. 76.5-77.5°, was 2.5 g. The mother liquor was left in a vacuum desiccator, and a further 0.21 g of material of the same melting point was isolated. The total yield of phenyllead triisobutyrate was 2.71 g (48.8%). A portion (0.5 g) was recrystallized, with careful heating, from 3 ml of dry hexane. Well formed crystals separated and were washed with hexane and dried (0.4 g, m.p. 77-78°). A further recrystallization from hexane did not affect the melting point.

Found %: Pb 38.04; 37.85

$C_{18}H_{26}O_6Pb$. Calculated %: Pb 37.99

The substance can be crystallized also from alcohol, but when the product is melted in a capillary a turbid melt is obtained.

II. Yellow mercuric oxide (2.16 g = one molecular proportion) was dissolved in 20 ml of isobutyric acid, and 5.32 g (one molecular proportion) of diphenyllead diisobutyrate was added; it dissolved readily. The reaction mixture was left for 12 days at room temperature. Phenylmercury chloride was separated as described above, and two thirds of the total amount of isobutyric acid was distilled from the filtrate at 2 mm and not above 40° (water bath). In the further treatment one of the following procedures was adopted. 1) The residue was transferred to a dish and left over caustic alkali in a vacuum desiccator. After eight days the precipitate formed was filtered off, washed with hexane, and dried as described above. The yield was 2.75 g (50.5%); m.p. 77-78°. 2) The residue was cooled in a mixture of ice and salt. The crystals that separated were filtered off and washed with hexane. The mother liquor was diluted with an equal volume of hexane and again cooled. The yield was somewhat lower with this procedure. Phenyllead triisobutyrate is a white crystalline substance, readily soluble in the cold in alcohol, acetone, chloroform, and benzene, and moderately soluble in the cold in hexane (readily soluble hot).

Phenyllead Tribenzoate

Phenyllead triisobutyrate (0.55 g = one molecular proportion) was added to a hot solution of 0.44 g (one molecular proportion + 20% excess) of benzoic acid in 8 ml of hexane. The solution was heated to the boil and set aside to crystallize. On the next day the precipitate formed was filtered off and washed successively with hot hexane, alcohol, and ether. The precipitate (0.4 g) was recrystallized from 1.5 ml of dry benzene, washed with hexane, and dried in a vacuum at 61° (jacket of chloroform vapor). The yield was 0.27 g (41.5%); m.p. 149.5-151°.

Found %: Pb 32.08; 32.07

$C_{27}H_{20}O_6Pb$. Calculated %: Pb 32.01

Phenyllead tribenzoate is a white crystalline substance, readily soluble in the cold in chloroform, ethyl acetate, and benzene. In alcohol it is moderately soluble cold, but readily soluble hot. It is insoluble in ligroin and hexane.

Benzeneplumbonic Acid

A solution of 0.27 g of phenyllead triisobutyrate in 5 ml of absolute alcohol was added dropwise under vigorous stirring to 6 ml of 5% ammonia. Reaction proceeded without appreciable rise in temperature. A yellowish amorphous precipitate appeared immediately. When the addition was complete, stirring was continued for three hours, and the reaction mixture was then set aside overnight. The precipitate was filtered off, carefully washed with water, with alcohol, and with ether, and then dried in a vacuum at 100° for one hour. The product was carefully ground and then further subjected to the same drying treatment for 80 minutes. The yield was 0.15 g (88.5%).

Benzeneplumbonic acid is a yellowish amorphous substance. It burns with a flash and a smoky flame, forming the yellow incrustation of lead oxides that is characteristic for organolead compounds. It is readily soluble in the cold in dilute hydrochloric acid, and it dissolves with difficulty in excess of concentrated (40-50%) caustic soda.

Found %: Pb 64.99; 65.58

$C_6H_6O_2Pb$. Calculated %: Pb 65.31

When dried as indicated above, benzeneplumbonic acid reacts gently with concentrated sulfuric acid (the first stage of analysis). When benzeneplumbonic acid that has not been dried sufficiently is mixed with sulfuric acid, it bursts into flame, and great care must therefore be taken in the early stages of mixing: a few drops of acid that has been cooled with ice and salt should first be added cautiously. When benzeneplumbonic acid is dried for a longer time, anhydride formation occurs. For example, after being dried under the same conditions for six hours, the material contains 66.47% of lead (the calculated amount for $C_6H_5PbO{\cdot}O{\cdot}{\cdot}PbOC_6H_5$ is 67.22%).

Benzeneplumbonic acid is readily soluble both in mineral and in organic acids. Benzeneplumbonic acid (0.2 g) was ground in the cold with 0.34 g (a two-fold excess) of isobutyric acid, and the solution obtained was left over caustic alkali in a vacuum desiccator. On the next day a small crystal of phenyllead triisobutyrate was added, and the reaction mixture solidified completely. The crystals were recrystallized from hexane and then melted at 77-78°. Phenyllead triisobutyrate obtained by the arylation of diphenyllead diisobutyrate melted at 77-78°. The melting point of a mixture of these preparations was not depressed.

Conversion of Phenyllead Triacetate into Phenyllead Triisobutyrate via Benzeneplumbonic Acid

A solution of 2 g of phenyllead triacetate in 30 ml of absolute alcohol was added dropwise with mechanical stirring to 50 ml of 5% ammonia. When addition was complete, the mixture was stirred for three hours and then set aside overnight. The precipitate formed was filtered off, washed successively with water, alcohol, and ether, and dried for one hour in a vacuum at 100°. The precipitate was ground in a mortar and then dried for one hour further under the same conditions. The yield was 0.9 g (66%).

A portion of the freshly prepared benzeneplumbonic acid (0.25 g = one molecular proportion) was ground with 0.24 g (3 molecular proportions + 15% excess) of isobutyric acid. The reaction mixture was diluted with benzene and filtered. The filtrate was transferred to a vacuum desiccator containing caustic alkali and paraffin wax (to remove solvents). The residue was a thick oil that crystallized out completely when a small crystal of phenyllead triisobutyrate was introduced. After one or two crystallizations from hexane, the substance melted at 77-78°. The previously prepared phenyllead triisobutyrate melted at 77-78°, and the melting point of a mixture of the two preparations was not depressed.

Some Properties of Phenyllead Triacetate and Triisobutyrate

When chloroform solutions of iodine and of either of these substances were mixed at room temperature, there was no decolorization and no decolorization occured when the mixture was boiled for some time. When the solution was left overnight, the color became weaker and a precipitate of lead iodide appeared, but even after 24 hours the solution still retained a definite feeble violet color. When phenyllead triacetate or triisobutyrate was boiled with water, hydrolysis occurred; the original crystalline material became amorphous, and the odor of the free organic acid appeared. At room temperature hydrolysis was slow. When the substance was left in the air for 5-6 days, its melting point became low and indefinite. The hydrolysis products (probably basic salts, which we have not yet investigated closely) readily passed into solution when 15-20% caustic alkali was added, and they also dissolved when acid was added; they did not dissolve in sodium carbonate solution, cold or hot. When phenyllead triacetate or triisobutyrate was hydrolyzed in the cold with 5% ammonia, the resulting freshly precipitated benzeneplumbonic acid dissolved smoothyl in 15-20% caustic alkali – behavior that contrasts with that of the dried acid (see above), which dissolves with difficulty.

Dearylation of Phenyllead Triisobutyrate with the Aid of Mercuric Isobutyrate

Phenyllead triisobutyrate (0.55 g = one molecular proportion) was warmed with 1.2 ml of isobutyric acid, and the resulting solution was mixed with a solution of 0.217 g (one molecular proportion) of yellow mercuric oxide in 0.8 ml of isobutyric acid. Reaction was slow, and the copper test for mercuric isobutyrate was positive; when water was added to a drop of the solution, no lead dioxide separated (absence of lead tetraisobutyrate in the mixture). After four days the test for the presence of mercuric ions was still positive, but a brown turbidity due to lead dioxide now formed when a drop of the reaction mixture was mixed with water. Well formed crystals gradually formed on the bottom of the flask. After ten days the reaction mixture was cooled with ice, and the precipitate was filtered off and washed with hexane. The yield was 0.2 g (36%); m.p. 114°. The melting point of lead tetraisobutyrate is 114° (see below), and a mixture with known lead tetraisobutyrate showed no melting point depression. The substance decomposed in the air, and it gave a brown precipitate of lead dioxide with water. Even after it had stood for ten days, the mother liquor still contained some mercuric isobutyrate.

Lead Tetraisobutyrate

A mixture of 17.6 g (one molecular proportion) of lead tetraacetate and 70 g (20 molecular proportions – five times the theoretical amount) of isobutyric acid was heated in a water bath in a round-bottomed flask carrying a column and arranged for vacuum distillation. The pressure was 12-15 mm, and the temperature of the bath was raised gradually to 70°. The reaction was carried out both without passage of air through the capillary leak, and also with passage of air, which, in order to avoid hydrolysis, had been first passed though a Tishchenko bottle containing sulfuric acid. The acetic acid and part of the isobutyric acid distilled over slowly, about 36 ml (half of the total volume of reaction mixture) being collected. Well formed crystals of lead tetraisobutyrate separated from the residue, when cool. These were filtered off through a funnel carrying a sintered-glass filter and protected from atmospheric moisture. They were washed with a little isobutyric acid, and isobutyric acid was removed with petroleum ether. The yield of lead tetraisobutyrate was 19 g (85.5%); it melted at 113-114° (Colson [13] gives 109°).

After being washed with petroleum ether, the substance was sufficiently pure and did not require recrystallization. However, when too much isobutyric acid was distilled off, the lead tetraisobutyrate obtained had a low melting point, and it had to be recrystallized from petroleum ether with the addition of a few drops of isobutyric acid (1 g of lead tetraisobutyrate was heated with 4 ml of petroleum ether).

Found %: Pb 36.92

$C_{16}H_{28}O_8Pb$. Calculated %: Pb 37.32

Lead tetraisobutyrate forms white crystals, and it is readily soluble in the cold in chloroform, dichloroethane, carbon tetrachloride, benzene, toluene, and xylene, but less soluble in isobutyric acid. It dissolves poorly in the cold, but readily when heated in petroleum ether and hexane; it is decomposed by water and by alcohol.

SUMMARY

1. By the dearylation of organolead compounds of formula Ar_2PbX_2, members of a new class of compounds, $ArPbX_3$, have been prepared for the first time (Ar is an aromatic radical, and X is the residue of an organic acid).

2. The properties and mutual transformations of phenyllead triacetate, phenyllead triisobutyrate, phenyllead tribenzoate, and benzeneplumbonic acid are described.

Received July 1, 1954

L. Ya. Karpov Physicochemical Institute

LITERATURE CITED

[1] E. M. Panov and K. A. Kocheshkov, Proc. Acad. Sci. USSR 85, 1037 (1952); J. Gen. Chem. 25, 489 (1955), T.p. 457)*.

[2] E. M. Panov and K. A. Kocheshkov, Proc. Acad. Sci. USSR 85, 1293 (1952).

[3] M. M. Nad and K. A. Kocheshkov, J. Gen. Chem. 12, 409 (1942).

[4] P. Austin. J. Am. Chem. Soc. 53, 1544 (1931).

[5] K. A. Kocheshkov, J. Russ. Phys. Chem. Soc. 61, 1385 (1929).

[6] G. Meyer, Ber. 16, 1442 (1883).

[7] J. Druce, Chem. News 120, 229 (1920).

[8] M. Lesbre, Comptes rend., 200, 559 (1935); 204, 1822 (1937); 206, 1481 (1938); 210, 535 (1940).

[9] G. Calingaert, H. Shapiro, F. Dykstra, L. Hess, J. Am. Chem. Soc. 70, 3902 (1948).

[10] V. V. Korshak and G. S. Kolesnikov, Tetraethyllead, State Chem. Tech. Press, Moscow, 1946, p. 37.

[11] H. Gilman, L. D. Apperson, J. Org. Chem. 4, 162 (1939).

[12] A. N. Nesmeyanov and K. A. Kocheshkov, J. Gen. Chem. 4, 1102 (1934).

[13] Colson, Comptes rend., 136, 1664 (1903).

---

* T.p. = C. B. Translation pagination

COMPOUNDS OF THE CLASSES Ar_2PbX_2 AND $ArPbX_3$ IN THE p-TOLYL SERIES

K. A. Kocheshkov and E. M. Panov

In the course of work on p-tolyl members of the new class of compounds $ArPbX_3$ (Ar is an aromatic radical and X is the residue of an organic acid) which we have discovered [1]

$$(p\text{-}CH_3C_6H_4)_2Pb(OOCCH_3)_2 + Hg(OOCCH_3)_2 \rightarrow p\text{-}CH_3C_6H_4Pb(OOCCH_3)_3 +$$
$$+\ p\text{-}CH_3C_6H_4HgOOCCH_3$$

we encountered difficulties associated with the synthesis of the starting substance Ar_2PbX_2.

It is stated in the literature [2] that di-p-tolyllead diacetate (or diformate) is formed by the action of the hot organic acid on tetra-p-tolyllead. It is known, however, that for phenyl homologs, compounds of the class Ar_4Pb can be obtained only by the further arylation of Ar_3Pb [3]:

$$Ar_3Pb \xrightarrow{Br_2} Ar_3PbBr \xrightarrow{ArMgX} Ar_4Pb.$$

It would obviously be irrational for our purpose to make use of this reaction and combine it with subsequent elimination of two aryl groups. We therefore investigated several possible methods for the direct conversion of Ar_3Pb into Ar_2PbX_2.

1. The direct action of organic acids at 120-140° on tri-p-tolyllead (which probably underwent disproportionation $4Ar_3Pb = 3Ar_4Pb + Pb$) gave only low yields.

2. Synthesis in accordance with the scheme $(p\text{-}CH_3C_6H_4)_3Pb \xrightarrow{I_2} (p\text{-}CH_3C_6H_4)_3PbI \xrightarrow{I_2} (p\text{-}CH_3C_6H_4)_2PbI_2 \xrightarrow{I_2}$ $\xrightarrow{NaOH} (p\text{-}CH_3C_6H_4)_2PbO \xrightarrow{CH_3COOH} (p\text{-}CH_3C_6H_4)_2Pb(OOCCH_3)_2$ has no advantage over the previous method, since the preparations of mono- and di-halides required separate stages. Moreover, the dihalides are of low solubility in organic solvents, and their conversion into the corresponding oxides is difficult.

3. We found that the most expedient method was as follows:

$$3(p\text{-}CH_3C_6H_4)_3Pb + 4HNO_3 \rightarrow 3(p\text{-}CH_3C_6H_4)_3PbNO_3 + NO + 2H_2O;$$
$$(p\text{-}CH_3C_6H_4)_3PbNO_3 + HNO_3 \rightarrow (p\text{-}CH_3C_6H_4)_2Pb(NO_3)_2 + CH_3C_6H_5;$$
$$(p\text{-}CH_3C_6H_4)_2Pb(NO_3)_2 + 2KOH \rightarrow (p\text{-}CH_3C_6H_4)_2PbO + 2KNO_3 + H_2O;$$
$$(p\text{-}CH_3C_6H_4)_2PbO + 2RCOOH \rightarrow (p\text{-}CH_3C_6H_4)_2Pb(OOCR)_2 + H_2O.$$

Unlike the corresponding dihalide, di-p-tolyllead dinitrate is soluble in hot alcohol and is readily converted by alcoholic caustic potash into the corresponding oxide, and then further into the salt Ar_2PbX_2.

In this way di-p-tolyllead diacetate (in 64% yield) and di-p-tolyllead diisobutyrate (in 48% yield) were prepared, and these substances were then applied in the preparation of p-tolyllead triacetate and p-tolyllead trimethacrylate.

EXPERIMENTAL

Di-p-tolyllead Diacetate

With constant shaking and over a period of 20-25 minutes 7.5 g (one molecular proportion) of tri-p-tolyllead [4] was added in small portions of 75 ml of concentrated nitric acid heated to the boiling point. Reaction was very vigorous – each fresh portion of tri-p-tolyllead caused foaming of the mixture with evolution of brown oxides of nitrogen. The nitric acid turned yellow, and precipitate of di-p-tolyllead dinitrate formed on the bottom of the flask. When the whole of the tri-p-tolyllead had been added, heating was continued for a few minutes, and the reaction mixture was then cooled. The di-p-tolyllead dinitrate was filtered off and washed with water.

This crude di-p-tolyllead dinitrate was heated with 80 ml of alcohol, and the solution so obtained was brought to the boil. A solution of 2.2 g (two molecular proportions + 20% excess) of caustic potash in 25 ml of ethanol was then added, and a yellowish precipitate formed, which was filtered off and washed successively with alcohol and ether. The product was 5.25 g of di-p-tolyllead oxide.

The unpurified di-p-tolyllead oxide (3.2 g) was mixed with 3 ml of glacial acetic acid (heat was evolved). In order to obtain more complete solution the mixture was warmed cautiously, but some undissolved material still remained. Ethyl acetate (15 ml) was added, and the mixture was heated to the boil and then filtered. The filtrate was cooled in a mixture of ice and salt, and 3.08 g (64% on the amount of tri-p-tolyllead taken) of di-p-tolyllead diacetate, m.p. 209-210°, was obtained. The substance was sufficiently pure: a further crystallization from ethyl acetate did not affect the melting point.

Found %: Pb 40.29; 40.67

$C_{18}H_{20}O_4Pb$. Calculated %: Pb 40.84

Di-p-tolyllead diacetate is a white crystalline substance, m.p. 209-210° (Polis [2] gives 195°). It is extremely soluble in the cold in chloroform and acetic acid, and it is very soluble in ethanol and methanol. It is moderately soluble in the cold in benzene, acetone, and ethyl acetate, but is readily soluble at a higher temperature. It is of very poor solubility in hexane and ether, even when hot.

Di-p-tolyllead Diisobutyrate

1. A mixture of 1.2 g (one molecular proportion) of tri-p-tolyllead and 2.2 g (10 molecular proportions) of isobutyric acid was heated at 120-140° for one hour. The resulting solution (better after dilution with an equal amount of hexane) after cooling yielded well formed crystals (0.41 g) melting at 198-202°. Recrystallization from benzene raised the melting point to 202-203° (yield 0.3 g). A second crystallization from benzene did not affect the melting point.

Found %: Pb 36.96; 36.90

$C_{22}H_{28}O_4Pb$. Calculated %: Pb 36.78

Determination of the Number of Acid Residues. For 0.0698 g of the substance, 2.85 ml of 0.1 N NaOH was required; 0.0698 g of di-p-tolyllead diisobutyrate is equivalent to 2.48 ml of 0.1 N NaOH.

2. A mixture of 4 g (one molecular proportion) of unpurified di-p-tolyllead oxide (see above) and 4 ml (about four molecular proportions) of isobutyric acid was prepared and was heated cautiously. Ethyl acetate (6 ml) was added, and the mixture was heated to the boil and then filtered from undissolved material. Crystals melting at 202-203° separated from the filtrate. In admixture with di-p-tolyllead diisobutyrate prepared as described above there was no depression of melting point. The yield was 2.7 g (48.3%).

Di-p-tolyllead diisobutyrate is extremely soluble in the cold in chloroform, and is very soluble in methanol, ethanol, and ethyl acetate. It is moderately soluble in the cold and very soluble at higher temperature in benzene, acetone, and carbon tetrachloride. It is insoluble in ether and hexane, even when hot.

p-Tolyllead Triacetate

Mercuric acetate (1.59 g = one molecular proportion) was warmed with 45 ml of glacial acetic acid, and to the resulting warm solution 2.5 g (one molecular proportion) of di-p-tolyllead diacetate (see above) was added; it dissolved very readily. After one day the copper-plate reaction for mercury ions was found to be negative. Dropwise addition was then made of 1.9 ml of alcoholic 2.62 N HCl (one molecular proportion). The precipitate that formed was found to be p-tolylmercury chloride, m.p. 238° (Nesmeyanov [5] gives 238-239°); the yield was 1.5 g (86%). The filtrate was left over caustic alkali in a vacuum desiccator to remove acetic acid. The residue was a thick oil, which crystallized when rubbed out. The yield of crude material was 2-2.2 g; it was recrystallized from 6 ml of hot freshly distilled ethyl acetate acidified with a drop of acetic acid, the solution being filtered and cooled in an ice-salt mixture. The yield was 1.6 g (67%) of p-tolyllead triacetate, m.p. 84-86°, raised to 86-88° by a second crystallization from hot ethyl acetate; in further recrystallizations the melting point remained constant.

Found %: Pb 43.19

$C_{13}H_{16}O_6Pb$. Calculated %: Pb 43.59

When crystallized from benzene, the substance separated with one molecule of solvent of crystallization.

The substance (1 g) was dissolved in hot benzene (3 ml). The solution was filtered and diluted with 3 ml of hexane. The crystals that separated (0.6 g) were vacuum-dried at 61° (jacket of chloroform vapor) for five minutes, and then at room temperature for 30 minutes.

Found %: Pb 37.60

$CH_3C_6H_4Pb(OOCCH_3)_3 \cdot C_6H_6$. Calculated %: Pb 37.49

The benzene of crystallization could be removed completely only by drying the finely ground material in a vacuum at room temperature for two days (Found %: Pb 43.44).

p-Tolyllead triacetate forms friable crystals, extremely soluble in the cold in methanol, ethanol, chloroform, and acetic acid. It is moderately soluble in the cold, and readily soluble at higher temperature, in ethyl acetate, acetone, and benzene; it is insoluble in hexane and ether, even when hot.

p-Tolyllead Trimethacrylate

p-Tolyllead triacetate (0.36 g = one molecular proportion) was dissolved in 1.5 ml of absolute alcohol, and the solution was filtered. Methacrylic acid (0.39 ml = six molecular proportions) was added to the filtrate, and the mixture was placed in ice and salt. After a few minutes well formed needles appeared, and these were filtered off and recrystallized from hexane. The yield was 0.17 g (42%).

Found %: Pb 37.31; 37.08

$C_{19}H_{22}O_6Pb$. Calculated %: Pb 37.44

At temperatures above 120° p-tolyllead trimethacrylate gradually decomposes without melting. It forms needle-like crystals, which are readily soluble in the cold in ethyl acetate, chloroform, and benzene. They are moderately soluble in the cold, and readily soluble at higher temperatures in methanol, ethanol, and acetone; they are poorly soluble in ether and hexane, even when hot.

p-Tolueneplumbonic Acid

A solution of 0.5 g of p-tolyllead triacetate in 10 ml of absolute alcohol was added dropwise with vigorous stirring to 12 ml of 5% ammonia. There was an immediate white amorphous precipitate. The reaction mixture was stirred for three hours and was then set aside overnight. The precipitated p-tolueneplumbonic acid was filtered off, carefully washed with water, with alcohol, and with ether (the substance yellowed somewhat on the filter), and then dried for one hour in a vacuum at 100°. The product was carefully ground and then dried further for one hour under the same conditions. The yield was 0.18 g (60%).

Found %: Pb 62.19; 62.52

$C_7H_8O_2Pb$. Calculated %: Pb 62.55

p-Tolueneplumbonic acid is a white or somewhat yellowish amorphous substance. It is readily soluble in the cold in dilute hydrochloric acid and also in organic acids; it dissolves with some difficulty in concentrated (40-50%) caustic alkali. When boiled with concentrated hydrochloric acid, it yields toluene (elimination of the tolyl group).

Conversion of p-Tolyllead Triacetate into p-Tolyllead Trimethacrylate via p-Tolueneplumbonic Acid

A solution of 0.5 g of p-tolyllead triacetate in 10 ml of absolute alcohol was added dropwise with vigorous stirring to 12 ml of 5% ammonia. There was an immediate white amorphous precipitate. The reaction mixture was stirred for three hours and was then set aside overnight. The precipitate formed was filtered off, washed with water, with alcohol, and with ether, and then dried in a vacuum at 100°. The freshly prepared p-tolueneplumbonic acid was ground with methacrylic acid, the mixture was diluted with benzene and filtered, and the filtrate was left in a vacuum desiccator to remove solvent. The residue was crystallized from hexane. The characteristic needles of the trimethacrylate were obtained.

Found %: Pb 37.08; 37.13

$C_{19}H_{22}O_6Pb$. Calculated %: Pb 37.44

SUMMARY

1. A method has been developed for the synthesis of compounds of the class Ar_2PbX_2 (Ar is an aromatic radical and X is the residue of an organic acid) from Ar_3Pb, the syntheses investigated being those of di-p-tolyllead diacetate and di-p-tolyllead diisobutyrate.

2. Members of a new class of compounds have been prepared, namely, p-tolyllead triacetate and p-tolyllead trimethacrylate, the latter being obtained from the former by a transacylation process.

3. A new areneplumbonic acid has been described, namely, p-tolueneplumbonic acid.

Received July 3, 1954

L. Ya. Karpov Physicochemical Institute

LITERATURE CITED

[1] E. M. Panov and K. A. Kocheshkov, Proc. Acad. Sci. USSR 85, 1037, 1293 (1952).

[2] A. Polis, Ber. 21, 3424 (1888).

[3] K. A. Kocheshkov, Synthetic Methods for Organometallic Compounds of Group IV Elements, Acad. Sci. USSR Press, Moscow and Leningrad, 1947, p. 88.

[4] H. Gilman, J. C. Bailie, J. Am. Chem. Soc. 61, 731 (1939).

[5] A. N. Nesmeyanov, J. Russ. Phys. Chem. Soc. 61, 1393 (1929).

FREE ENERGY CHANGE IN THE ADSORPTIONAL DISPLACEMENT OF BUTENE BY WATER FROM A CATALYST SURFACE

A. A. Balandin, O. K. Bogdanova, and A. P. Shcheglova

In the study of the action of catalysts it is important to know the properties of the intermediate adsorption complex formed between a reacting substance and the catalyst. Such properties include the adsorption coefficient of the substance for the catalytically active surface, and we have previously examined an experimental method for the determination of this property [1, 2].

The adsorption coefficient a is simply the adsorption equilibrium constant, and the quantity z, which has been called the relative adsorption coefficient, is the equilibrium constant for the adsorptional displacement of one substance by another from the active surface.

We shall denote the total number of like catalytically active centers on the given surface by s, and by s_0, s_1, $s_2, \ldots, s_n$ we shall denote the numbers of these centers in the free state (s_0) and occupied each by a single molecule of the substances $A_1, A_2, \ldots, A_n$, respectively, derived from the gas phase. The ratios

$$\left.\begin{aligned} N'_0 &= s_0/s \\ N'_1 &= s_1/s \\ N'_2 &= s_2/s \\ &\vdots \\ N'_n &= s_n/s \end{aligned}\right\} \qquad (1)$$

will be the mole fractions of free centers and adsorption complexes on the surface. By $N_1, N_2, \ldots, N_n$ we shall denote the mole fractions of the substances $A_1, A_2, \ldots, A_n$ in the gas, which has a total pressure of P, and by k_1, $k_2, \ldots, k_n$ we shall denote the rate constants for adsorption, and by $k_{-1}, k_{-2}, \ldots, k_{-n}$ the rate constants for desorption. For adsorption equilibrium, equating rates of adsorption and desorption, we have:

$$\left.\begin{aligned} k_1N_1PN'_0 &= k_{-1}N'_1 \\ k_2N_2PN'_0 &= k_{-2}N'_2 \\ \cdots&\cdots\cdots \\ k_nN_nPN'_0 &= k_{-n}N'_n \end{aligned}\right\} \qquad (2)$$

$$N'_1 + N'_2 + \ldots N'_n + N'_0 = 1 \qquad (3)$$

It can be readily shown from Equation 2 that the adsorption equilibrium constants $a_1, a_2, \ldots, a_n$ are given by

$$\left.\begin{aligned} a_1 &= \frac{k_1}{k_{-1}} = \frac{N'_1}{N_1N'_0} \cdot \frac{1}{P} \\ a_2 &= \frac{k_1}{k_{-2}} = \frac{N'_2}{N_1N'_0} \cdot \frac{1}{P_1} \\ &\cdots\cdots\cdots\cdots \\ a_n &= \frac{k_n}{k_{-n}} = \frac{N'_n}{N_nN'_0} \cdot \frac{1}{P} \end{aligned}\right\} \qquad (4)$$

These adsorption equilibrium constants $a_1, a_2, \ldots, a_n$ are equal to the ratios of adsorption and desorption rate constants and refer, respectively, to the following dynamic equations:

$$\left.\begin{array}{l} A_1\,(\text{gas}) + S\,(\text{surf.}) = A_1{\cdot}S\,(\text{surf.}) \\ A_2\,(\text{gas}) + S\,(\text{surf.}) = A_2{\cdot}S\,(\text{surf.}) \\ \cdots\cdots\cdots\cdots\cdots\cdots \\ A_n(\text{gas}) + S\,(\text{surf.}) = A_n{\cdot}S\,(\text{surf.}) \end{array}\right\} \qquad (5)$$

In these equations $A_1{\cdot}S$, $A_2{\cdot}S$, . . . , $A_n{\cdot}S$ denote adsorption complexes. The quantities a_1, a_2, . . . , a_n can be regarded also simply as Langmuir adsorption coefficients. In fact, Equations 4 give

$$\left.\begin{array}{l} N'_1 = a_1N_1PN'_0 \\ N'_2 = a_2N_2PN'_0 \\ \cdots\cdots\cdots \\ N'_n = a_nN_nPN'_0. \end{array}\right\} \qquad (6)$$

Associating with these the identity

$$N'_0 = N'_0 \qquad (7)$$

and adding these equations (6 and 7), we find, with the help of Equation 3 that

$$1 = (a_1N_1P + a_2N_2P + \ldots + a_nN_nP + 1)N'_0. \qquad (8)$$

Determining the value of N'_0 from Equation 8 and substituting it in the first of Equations 6, we arrive at Langmuir's isotherm for a mixture

$$N'_1 = \frac{a_1N_1P}{1 + a_1N_1P + a_2N_2P + \ldots + a_nN_nP}. \qquad (9)$$

We find, therefore, that the equilibrium constants a_1, a_2, . . . , a_n are indeed adsorption coefficients.

As is well known, mole fractions, partial pressures p, and concentrations [A] are related together, for each component of a gas mixture, by an equation of the type

$$N_1P = p_{A_1} = [A_1]RT. \qquad (10)$$

By substituting this in Equation 9 we can express the isotherm in other variables — partial pressures or concentrations. It should be noted that each term of the denominator (and also numerator) of Equation 9 is dimensionless, so that the dimensions of the constant coefficients in the terms of the denominator must be the inverse of those of the corresponding variables.

At sufficiently high pressures or concentrations we can neglect the term unity in the denominator of Equation 9. It will be obvious that the constant coefficients will retain their values irrespective of which variable, N, P, or [A], is chosen for the expression of the isotherm. Taking concentration as the variable we obtain

$$N'_1 = \frac{a_1[A_1]}{a_1[A_1] + a_2[A_2] + \ldots + a_n[A_n]}. \qquad (11)$$

Division of numerator and denominator by a_1 yields

$$N'_1 = \frac{[A_1]}{[A_1] + z_2[A_2] + \ldots + z_n[A_n]} \qquad (12)$$

in which z_2, . . . , z_n are dimensionless quantities, namely, relative adsorption coefficients:

$$\left.\begin{array}{l} z_2 = a_2/a_1 \\ \cdots\cdots\cdots \\ z_n = a_n/a_1 \end{array}\right\} \qquad (13)$$

In order to bring out their physical meaning, we will substitute the values of a_1, a_2, . . . , a_n from Equation 4 into Equation 13:

$$z_2 = \frac{N'_2N_1}{N'_1N_2}, \qquad (14)$$

which is simply the equilibrium constant for the process of the adsorptional displacement of the substance A_1 from the surface by the substance A_2:

$$A_1{\cdot}S\,(\text{surf.}) + A_2\;(\text{gas}) = A_2{\cdot}S\,(\text{surf.}) + A_1(\text{gas}) \qquad (15)$$

and in general

$$z_n = \frac{N'_n N_1}{N'_1 N}, \tag{16}$$

which is the equilibrium constant for the process:

$$A_1 \cdot S(\text{surf.}) + A_n(\text{gas}) = A_n \cdot S(\text{surf.}) + A_1(\text{gas}) \tag{17}$$

Since $a_1, a_2, \ldots, a_n$ and $z_2, \ldots, z_n$ are equilibrium constants, a treatment based on chemical thermodynamics will lead us to free energies.

It will be seen that the standard free energy for the formation of adsorption complexes from the substances $A_1, A_2, \ldots, A_n$ in the gas state and the free surface will be

$$\left.\begin{array}{l} \Delta F^\circ(A_1) = -RT \ln a_1, \\ \Delta F^\circ(A_2) = -RT \ln a_2, \\ \cdots\cdots\cdots\cdots\cdots \\ \Delta F^\circ(A_n) = -RT \ln a_n, \end{array}\right\} \tag{18}$$

in which the free energies correspond line by line to the processes of Equation 5.

The standard free energies of displacement are

$$\left.\begin{array}{l} \Delta F^\circ(A_2, A_1) = -RT \ln z_2, \\ \cdots\cdots\cdots\cdots\cdots \\ \Delta F^\circ(A_n, A_1) = -RT \ln z_n, \end{array}\right\} \tag{19}$$

in which $\Delta F^\circ(A_2, A_1)$ and $\Delta F^\circ(A_n, A_1)$ refer to the processes of Equations 15 and 17, respectively.

It is of interest to note that the quantities $\underline{z}$ (owing to their zero dimensions), and also the free energies of displacement derived from them, are invariant quantities with respect to change of variable ($\underline{N}$, $\underline{P}$, or [A]) and with respect to change in the units in which the adsorption coefficients are measured. On the other hand, in Equations 18, which involve $\underline{a}$, such changes (if any desired pressures are considered) result in the appearance of constant terms, which determine the standard state.

Finding now from Equation 1 not the fraction of the surface N_1', but the actual surface s_1 occupied by the reacting substance A_1, and assuming the rate of reaction dx/dt to be proportional to the latter, we obtain the kinetic equation

$$\frac{dx}{dt} = k\frac{[A_1] + z_2}{[A_1] \quad z_2[A_2] + \ldots + z_n[A_n]} \tag{20}$$

in which $\underline{k}$ is the rate constant for the catalytic reaction and includes the value of the active surface. It should be noted that in the derivation no limitation has been placed on the number of substances $\underline{n}$.

Hence, by determining relative adsorption coefficients from kinetic measurements carried out by the method that we have developed [1], we are able to determine experimentally the standard free energies of displacement for the actual active catalytic centers (not merely for the total surface of the catalyst). Similarly, basing our calculations on Equation 9 instead of Equation 12, we may determine the standard free energies of adsorption on the catalytically active centers.

As an example of the application of these views, we consider below the effect of water vapor on the dehydrogenation of butene to butadiene. In a previous investigation [1] we have studied the kinetics of the catalytic dehydrogenation of butene to butadiene and have developed an experimental method that enables us to exclude a number of complicating factors from consideration, one of these being the ready polymerization of butadiene with the formation of a carbonaceous film that poisons the catalyst. It was found that the rate of dehydrogenation is not greatly dependent on pressure, the lowering of which reduces the rate of polymerization. The kinetic equation for the dehydrogenation reaction was found, and the relative adsorption coefficients were measured. It was found that the relation between the adsorption coefficients of butene, butadiene, and hydrogen at 560° could be expressed as 1 : 9.5 : 0.8. It was shown that the formula for the determination of adsorption coefficients actually did give fairly constant values of $\underline{a}$, independent of concentrations.

In the present investigation it was first of all necessary to determine what type of poisoning occurred – permanent or temporary – when water vapor was introduced. If temporary, then the method of determining adsorption coefficients and free energies of adsorptional displacement could be applied, but if permanent, another approach would be required (see below).

EXPERIMENTAL

The rates of dehydrogenation in various binary mixtures of butene and water vapor were measured. In order to determine the extent to which butadiene underwent decomposition, the behavior of binary mixtures of butadiene and water vapor was also studied, and other experiments were carried out on the dehydrogenation of butene over a catalyst that had been previously treated with water vapor.

Experimental Procedure

The experiments were carried out by the flow method in the apparatus described previously [1], the only modification being the addition of a definite amount of water vapor to the butene (or butadiene) just before it entered the furnace. For this purpose, after passing through the flowmeter, gas from the gas holder entered a saturator containing water, which consisted of a cylinder provided with an electric spiral for the heating of the water, a thermometer, a buret containing water for the maintenance of the level in the saturator, and two tubes for entry and exit of gas. The gas from the saturator passed directly into a silica tube heated in an electric furnace. The exit gases from the furnace passed to a receiver fitted with a spherical condenser, in which the water vapor condensed, and were collected in a gas holder over saturated brine.

The temperature in the catalyst layer was measured by means of a nichrome-constantan couple contained in a silica pocket, the readings being taken on a potentiometer, and the temperature was maintained constant within ± 0.25°. The rate of passage of gas was determined by a flowmeter and was constant throughout an experiment. The degree of saturation of the butene (or butadiene) with water vapor was determined from the vapor pressure at the given temperature and, when possible, it was determined also from the weight of water collected in the receiver.

The experiments were carried out with 2 ml of chrome catalyst and 4 ml of silica (crushed quartz), which was placed in front of the catalyst to aid in the heating of the gas. After each experiment the catalyst was treated in a stream of air at 600°. Just before the experiment nitrogen was passed for three minutes in order to displace air from the apparatus. The sampling of gas for analysis was carried out three minutes after the beginning of the experiment.

The volumes of the gases were reduced to standard conditions. In the gas collected, butadiene was determined by its reaction with maleic anhydride, butadiene together with butene by absorption in 84% sulfuric acid, ethylene by absorption in a solution of mercuric sulfate in sulfuric acid, hydrogen and saturated hydrocarbons by combustion over copper oxide. In some experiments the exit gases were tested for carbon monoxide with ammoniacal cuprous chloride. Neither carbon monoxide nor carbon dioxide was detected in the gases, thus indicating that there was no chemical interaction between the hydrocarbons and water under the given conditions.

The butene was prepared from butyl alcohol and was purified by fractionation through a Davis column. The source of the butadiene was the butadiene fraction obtained from the SK works; it was purified from higher hydrocarbons and had the following composition: 90.8-91% of butadiene and 9-9.2% of butene.

Experimental Results and their Discussion

The experiments with mixtures of butene and water vapor were carried out at 560°, 580°, and 600° at a space velocity of 16,000 liters per liter per hour. The extent of dilution of butene with water vapor was varied from 9 to 75% by volume. The amount of butadiene formed under all these conditions was determined, and the reaction products were also analyzed by the methods indicated above. The results obtained are collected together in Table 1, in which they are arranged so that experiments at any given temperature are in order of increasing water content in the mixture. A control experiment was carried out at the end of every series.

Fig. 1 shows the dependence of the amount of butadiene formed in unit time (five minutes) on the composition of the butene-water mixture used. Fig. 2 shows similar results for the dependence of the amount of hydrogen formed on the composition of the original butene-water mixture. The corresponding curves of Figures 1 and 2 are very similar, indicating that the extent to which secondary decomposition reactions occured was not great. The form of the curves indicates that water is adsorbed more strongly than butene. All of the curves fall below the additive straight line. We applied the theoretical considerations that we developed in a previous paper [2] to the data obtained, and we calculated the relative adsorption coefficient of water molecules (z) from the formula derived from these considerations [1]

$$Z = \frac{\frac{m_0}{m} - 1}{\frac{100}{p} - 1}, \tag{21}$$

in which p is the mole percentage of butene in its binary mixture with water, m_0 is the rate of dehydrogenation of pure butene, and m is the same for the p% mixture under the same conditions. Results of calculations from Equation 21 are given in the last column of Table 1.

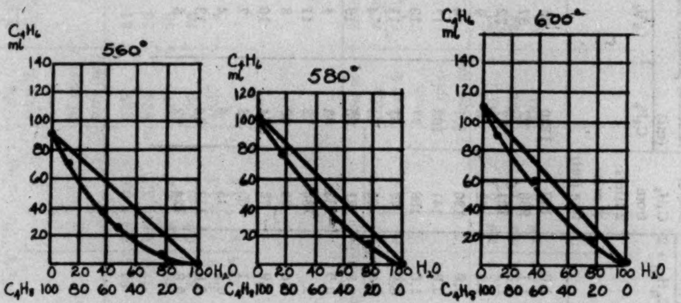


Fig. 1

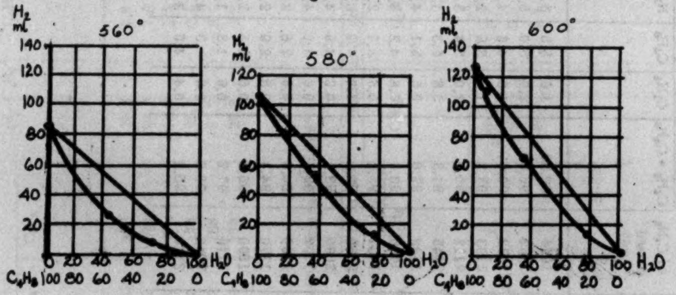


Fig. 2

It will be seen from Table 1 that in experiments at a given temperature the value of z is fairly constant, thus confirming the applicability of the theory. With rise in temperature, z falls: for a wide range of temperature we find that z is 3.1 (for 560°) and 2.0 (for 600°). The rate of fall of z apparently diminishes with rise in temperature, but the sensitivity of the method is such that over a narrower range of temperatures – 600° and 580° – the values of z practically coincide. By the application of Equation 7 to these data we may find the free energy of the displacement of butene from the active surface by water. It is found that for this process

$\Delta F^\circ = -4308$ cal/mole at 833°K

$\Delta F^\circ = -2702$ cal/mole at 853°K

TABLE 1

2 ml of catalyst + 4 ml of crushed quartz; time of contact τ = 0.06 sec.

Experiment No.	Temperature of experiment (°C)	Composition of mixture (% by volume)		Amount of C_4H_8 passed (ml)	Analysis of gas (% by volume)*					Loss of C_4H_8 from 2 liters of mixture (ml)	Reaction products from 2 liters of mixture (ml)				Relative adsorption coefficient z
		C_4H_8	H_2O		$C_4H_8 + C_4H_6$	C_2H_4	C_4H_6	H_2	C_nH_{2n+2}		C_4H_6	C_2H_4	H_2	C_nH_{2n+2}	
832	600	100	-	1654	89.80	1.6	5.5	5.8	1.0	149	1130	35	128	22	
833	600	90	10	1863	90.00	2.0	5.0	5.5	1.1	230	92	37	108	20	2.2
834	600	63.7	36.3	1863	90.6	1.6	4.6	4.6	1.1	121	57	22	62	15	1.7
835	600	25.0	75.0	1793	93.2	1.8	3.6	2.8	1.2	32	16	9	14	5	2.0
836	600	100	-	2112	90.0	2.0	5.4	5.2	0.9	190	107	44	111	19	Mean 2.0
827	580	100	-	2045	91.8	0.8	5.3	4.9	0.9	141	103	17	105	19	
828	580	82	18	1839	92.0	0.8	5.1	4.9	1.0	156	77	13	82	17	(1.5)
829	580	63.5	36.5	1786	93.4	0.8	4.2	3.7	0.9	77	51	11	51	12	1.8
830	580	26.0	74	1737	95.2	0.8	3.1	2.1	1.0	20	14	4	11	5	2.0
831	580	100	-	2065	93.2	1.0	4.9	3.8	0.8	121	95	16	80	17	Mean 1.9
820	560	100	-	2090	93.8	0.2	4.9	4.2	0.9	133	93	4	88	19	
823	560	91	9	1790	92.6	0.6	4.2	4.2	1.	135	72	11	87	23	3.0
822	560	66.3	33.7	1760	94.6	0.6	2.6	2.6	2.6	74	38	8	61	13	3.2
824	560	65.0	35	1770	94.4	0.8	2.9	2.9	0.9	75	34	10	37	13	3.0
821	560	59	41	1900	95.0	0.6	2.5	2.0	1.1	62	26	7	24	16	3.5
825	560	29	71	1716	97.2	0.6	1.3	1.1	0.6	15	8	4	7	4	Mean 3.1
826	560	100	-	2043	93.8	0.6	.3	4.4	0.8	113	84	13	95	18	
837	560	100	-	2120	95.2	0.4	4.6	3.1	0.8	124	92	8	64	16	

---

* No CO_2 was found in the gas.

TABLE 2

2 ml of catalyst + 4 ml of crushed quartz; temperature 600°

Experiment No.	Dilution with water vapor		Composition of initial gas (ml)		Analysis of gas (% by volume)					Loss of C_4H_6 from 2 liters of mixture (ml)	Reaction products from 2 liters of of mixture (ml)			
	Amount of hydrocarbons (%)	Amount of water (%)	C_4H_6	C_4H_8	$C_4H_8+C_4H_6$	C_2H_4	C_4H_6	H_2	C_nH_{2n+2}		C_4H_8	C_2H_4	H_2	$C_nH_{2n} = 2$
838	Without dilution		1930	192	96.8	0.8	81.5	0.6	0.8	538	61	12	9	12
840	93.2	6.8	1721	174	94.0	1.0	77.6	1.6	1.1	624	55	14	22	15
839	90.4	9.6	1707	173	95.8	1.0	78.2	1.4	0.9	547	78	13	19	13
841	68.3	31.7	1715	174	96.2	0.6	83.6	0.7	0.9	293	23	7	8	10
842	60.6	40.3	1662	168	97.2	0.4	86.8	-	1.1	156	3	5	-	14
843	25.0	75.0	1670	170	97.8	0.2	88.6	-	1.1	10	-	2	-	5

TABLE 3

2 ml of catalyst + 4 ml of crushed quartz; temperature 580°

Experiment No.	Dilution with water vapor		Composition of initial gas (ml)		Analysis of gas (% by volume)					Loss of C_4H_8 from 2 liters of mixture (ml)	Reaction products from 2 liters of of mixture (ml)			
	Amount of hydrocarbons (%)	Amount of water (%)	C_4H_8	C_4H_6	C_4H_8	C_2H_4	C_4H_6	H_2	C_nH_{2n+2}		C_4H_6	C_2H_4	H_2	C_nH_{2n+2}
827	Without dilution		2045	11	91.8	0.8	5.3	4.9	0.9	141	103	17	105	19
828	82.0	18	1839	9	92.0	0.8	5.1	4.8	1.0	185	94	16	99	21
846	Without dilution		1895	11	93.2	0.8	5.6	4.8	0.9	184	104	17	100	18 with preliminary treatment with water vapor

In a similar way, applying the same formula (Equation 7) to the results obtained previously [1] [$z_2 = 9.5$ for equilibrium constants for the displacement of butene by butadiene, and $z_3 = 0.82$ for the displacement of butene by hydrogen (at 560°)], we find that the free energies of the adsorptional displacement of butene by butadiene and of butene by hydrogen are given, respectively, by

$$\Delta F_2^\circ = -8572 \text{ cal/mole}$$
$$\Delta F_3^\circ = -755 \text{ cal/mole}$$

The results show that, owing to adsorptional displacement water vapor should retard the dehydrogenation of butene to butadiene. The adsorption coefficient of water on the active centers of the dehydrogenation catalyst is found to be 2.0-3.1 times as great as that of butene. Rise in temperature should accelerate the dehydrogenation of butene, not only as a result of the usual increase in rate constant with temperature, but also as a result of the reduction in the value of $z = a_{H_2O}/a_{C_4H_8}$. All this is in accord with the experimental facts.

The theory is therefore applicable quantitatively for catalytic dehydrogenation centers. Temporary poisoning does indeed occur in the process under consideration. Dehydrogenation, however, is not the only reaction promoted by the catalyst: there are other active centers on the surface [3], and on these occur the polymerization and decomposition of butadiene with formation of products giving a carbonaceous film. These reaction products slowly migrate to the dehydrogenation centers and cause poisoning that is no longer temporary, but permanent. It is therefore necessary to consider also the action of water vapor on the complicating reactions accompanying dehydrogenation. This action is fairly complicated.

When the results are applied to the determination of the amount of butene decomposed in its relation to the water content of the mixture, we obtain the curves shown in Fig. 3. It will be seen that the addition of 10% of water vapor causes the decomposition to be greater than that of pure butene, but as the dilution of butene with water is increased further the extent of decomposition diminishes and, at 70-75%, becomes less than one-half of that found for pure butene.

Thus, the curve for the total amount of butene decomposed passes through a maximum at 10% of water. As the temperature rises, this maximum becomes higher. Analysis of the reaction products showed that in the region of the maximum there was a small rise in the content of saturated hydrocarbons. This rise, however, can be neglected, for the principal by-products are liquid polymerization and, possibly, dimerization products. With increased dilution the amount of liquid products diminishes. In the gaseous products – apart from butadiene, butene, and hydrogen – ethylene (0.4-2.0%) and saturated hydrocarbons (0.8-2.0%) were found. The distribution of the reaction products at different temperatures can be seen from Fig. 3.

Further experiments were carried out with mixtures of butadiene and water vapor (Table 2). The extent of dilution with water vapor was varied over almost the same range as in the case of butene, namely 6-75% by volume. The rate of passage was as before. The experiments were carried out at 600°. Like butene, butadiene gave a decomposition peak at about 10% of water. With increase in dilution, the extent of decomposition decreased. The main decomposition products of butadiene were liquids. In the exit gases small amounts of ethylene (up to 1%), hydrogen (0-1.6%), and saturated hydrocarbons (0.8-1.3%) were detected.

The experiments with butadiene show quite clearly that in the presence of a chrome catalyst small amounts of water vapor encourage the formation of liquid reaction products – products of the condensation of butadiene. This is a new fact, deserving of further study. At a higher content of water vapor, the water molecules cover the catalyst surface, screening the active centers, and they distribute themselves over the surface between the butadiene molecules. As a result, polymerization and dimerization are retarded, for these processes require the proximity of two butadiene molecules on the surface.

Hence, in the process under consideration on the given catalyst water vapor acts in several directions. First, reversible poisoning occurs: a) water displaces butene from the surface, which is unfavorable for the dehydrogenation of butene; b) water displaces butadiene (from other sites on the surface), which is favorable for dehydration since polymerization is suppressed. Second, as a result of the last effect, water suppresses the irreversible poisoning of the active dehydrogenation centers by polymerization products. Third, , at low water concentrations an interesting phenomenon is observed – increased formation of liquid reaction products.

To determine the effect of water vapor on the catalyst surface, we carried out a pretreatment in which the catalyst was saturated with vapor. Just before the experiment nitrogen containing 10% of water vapor was passed over the catalyst for eight minutes. The mixture of butene and water vapor was passed for three minutes, and this was followed by undiluted butene that had been dried over calcium chloride. The results showed that this preliminary treatment with water vapor had no apparent effect on the catalyst surface. As will be seen from Table 3,

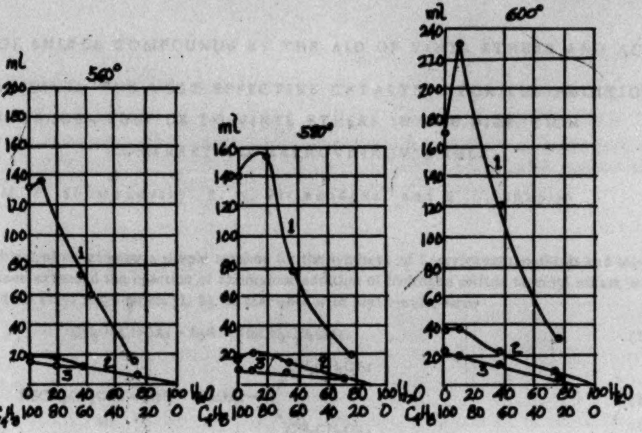


Fig. 3. 1) C_4H_8; 2.) saturated hydrocarbons; 3.) C_2H_4

Experiment 846, which was carried out at 580°, gave the same results as an experiment in which there was no preliminary treatment with water vapor. Hence, water vapor does not produce any irreversible poisoning or other change in the given catalyst.

SUMMARY

1. A method is proposed for the determination of equilibrium constants for the adsorptional displacement of some substances by others from a catalytically active surface; it yields also the free energies of the processes, and these determine the stability of the intermediate adsorption complexes.

2. It has been found that water vapor effects the adsorptional displacement of butene from the catalyst surface. The relative adsorption coefficient is about 3.1 at 560° and diminishes with rising temperature, attaining the value of 2.0 at 600°. The free energy of displacement of butene by water from the active catalyst surface is −4308 cal/mole at 833° K. and − 2702 cal/mole at 853° K. Moreover, water vapor suppresses the conversion of butadiene into polymerization products, which give resinous films on the catalyst and so poison it irreversibly.

3. We have observed an interesting, previously undescribed example of the acceleration of the condensation of butadiene on the catalyst surface under the influence of small addition (about 10%) of water vapor. It was established that, under these conditions, water vapor itself would not bring about irreversible poisoning of the catalyst.

Received August 15, 1954

N. D. Zelinsky Institute of Organic Chemistry of the
USSR Academy of Sciences

LITERATURE CITED

[1] A. A. Balandin, O. K. Bogdanova, and A. P. Shcheglova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1946, No. 5. 497.

[2] A. A. Balandin. J. Gen. Chem. 12, 160 (1942).

[3] A. A. Balandin, N. D. Zelinsky, O. K. Bogdanova, and A. P. Shcheglova, J. Appl. Chem. 15, 123 (1942).

BLANK
PAGE

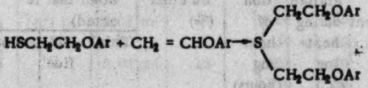
SYNTHESIS OF SULFUR COMPOUNDS BY THE AID OF VINYL ETHERS AND ACETYLENE

COMMUNICATION 12. THE MOST EFFECTIVE CATALYSTS FOR THE ADDITION OF HYDROGEN SULFIDE TO VINYL ETHERS IN THE DIRECTION CONTRARY TO MARKOVNIKOV'S RULE

M. F. Shostakovsky, E. N. Prilezhaeva, and E. S. Shapiro

With the object of developing a simple method for the synthesis of 2-aryloxyethanethiols and bis-(2-aryloxyethyl) sulfides, we have extended the reaction of anomalous addition of hydrogen sulfide to vinyl ethers, which we have previously studied for alkyl vinyl ethers [1, 2], to reactions with aryl vinyl ethers:

$$CH_2 = CHOAr + H_2S \rightarrow HSCH_2CH_2OAr \qquad (1)$$



$$HSCH_2CH_2OAr + CH_2 = CHOAr \rightarrow S\begin{matrix} CH_2CH_2OAr \\ CH_2CH_2OAr \end{matrix} \qquad (2)$$

The ethers investigated were phenyl vinyl ether and p-tert-butylphenyl vinyl ether.

The reaction proceeded very slowly with these ethers, and the catalysts that we had used in the previous investigations – traces of oxygen, a solution of HCl in dioxane – were found to be very ineffective. Also, long heating at fairly high temperatures did not give a satisfactory yield of the reaction products. When we carried out the reaction with alkyl vinyl ethers in presence of these catalysts [2], the products were 2-alkoxyethanethiol and a mixture of bis(2-alkoxyethyl) sulfide and 1-alkoxyethyl 2-alkoxyethyl sulfide in various proportions. This indicated that some of the hydrogen sulfide molecules added to the vinyl ether in the direction required by Markovnikov's rule. Aryl vinyl ethers, however, showed specific behavior in this reaction: unlike alkyl vinyl ethers, they reacted, under comparable conditions, exclusively in the direction contrary to that required by Markovnikov's rule, with formation of the pure isomers indicated in Equations 1 and 2.

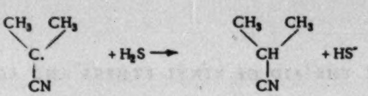
In earlier work Shostakovsky and Bogdanova have shown that the reactivity of aryl vinyl ethers in reactions proceeding under the influence of ionic catalysts is considerably less than that of alkyl vinyl ethers. For phenyl vinyl ether, for example, it is more difficult to effect hydrolysis and hydrohalogenation [3, 4], addition of alcohols, and the decomposition of its α-halogen derivatives [5]. Aryl vinyl ethers are considerably less active in polymerization reactions in presence of ionic catalysts [6, 7]. We have recently shown [8] that the polymerization of aryl vinyl ethers can be brought about by radical catalysts, though the yield is very low.

The results of the work cited above and of our work in the present investigation show beyond doubt that, irrespective of the mechanism by which they proceed, the addition reactions of aryl vinyl ethers are much slower than the corresponding reactions of alkyl vinyl ethers.

It was considered to be necessary to find other catalysts of the radical type to accelerate the anomalous addition of hydrogen sulfide to aryl vinyl ethers. First of all we tried ascaridole, which has been shown to accelerate reaction with butyl vinyl ether greatly, even at room temperature [1]. With this catalyst only phenyl vinyl ether gave a satisfactory yield of reaction products.

It was found that the most effective catalyst was 2,2'-azobis[2-methylpropionitrile], which is well known as an extremely active initiator for free-radical polymerization processes – it was in the presence of this catalyst that radical polymerization of vinyl ethers was first effected [9]. As regards the use of the azo nitrile as a catalyst in free-radical addition reactions, the only literature reference is in a patent [10] relating to reaction between olefins and hydrogen sulfide.

2,2'-Azobis[2-methylpropionitrile] decomposes in a known manner [11] into free radicals. In our case such a radical will probably attack hydrogen sulfide, and a chain reaction will begin, the first stage of which may be represented as



The thiol radical so formed will then enter into the process in accordance with the scheme given in one of our earlier communications [1].

Unlike ascaridole, 2,2'-azobis[2-methylpropionitrile] can be used to effect the quantitative addition of hydrogen sulfide, not only to phenyl vinyl ether, but also to p-tert-butylphenyl vinyl ether, so that 2-aryloxyethanethiols and bis(2-aryloxyethyl) sulfides can be synthesized in a comparatively simple way from readily accessible materials.

TABLE 1

Effect of Various Catalysts on the Addition Reaction between Hydrogen Sulfide and Butyl Vinyl Ether

Experiment No.	Amount of H_2S (moles per mole of ether)	Experimental conditions: Catalyst: Name	Catalyst: Amount (% by weight on ether)	Duration of experiment (days)	Temperature during heating (°C)	Duration of heating (hours)	Unchanged ether (%)	Yield of reaction products (% on ether that reacted): Thiol	Sulfide	Total	Content of 1,2'-isomer in sulfide fraction (%)
103	0.3	Oxygen	Traces	2	-	-	98	-	-	-	-
91	0.5	"	"	13	-	-	35.4	27.7	6.27	90.4	2.5
14	1.0	"	"	7	60	30	-	52.6	43.4	96.0	20.0
26	0.4	HCl in dioxane	0.09	2	-	-	49.5	15.2	70.7	85.9	9.0
3	1.3		0.1	1	70	8	-	54.3	36.8	91.1	31.8
101	2.1	Ascaridole	1.5	2	-	-	6.0	77.0	13.8	90.8	1.5
94	0.4	Azonitrile	0.2	2	-	-	37.0	23.8	74.5	98.3	-
95	0.4		0.2	2	60	14	19.0	-	98.0	98.0	-
93	2.2	"	0.2	2	-	-	-	79.0	12.8	91.8	2

TABLE 2

Effect of Various Catalysts on the Addition Reaction between Hydrogen Sulfide and Cyclohexyl Vinyl Ether

Experiment No.	Amount of H_2S (moles per mole of ether)	Experimental conditions: Catalyst: Name	Catalyst: Amount (% by weight on ether)	Duration of experiment, (days)	Temperature during heating (°C)	Duration of heating (hours)	Unchanged ether (%)	Yield of reaction products (% on ether that reacted): Thiol	Sulfide	Total	Content of 1,2'-isomer in sulfide fraction (%)
1	1.2	Oxygen	Traces	150	-	-	33.3	65.8	20.3	86.1	88.6
10	1.0	"	"	35.	60-65	245	-	16.5	48	64.5	91.7
4	0.9	HCl in dioxane-	0.08	12	60	63	-	19.7	37.4	57.1	104.4
13	1.5	Ascaridole	1.0	7	60-62	37	-	70.3	23.5	93.8	20.4
14	0.5		1.0	7	60-62	45	50	30.5	55.2	85.7	13.1
11	1.2	Azonitrile	0.2	7	-	-	-	28.9	67.5	95.4	5.8
12	0.5		0.2	7	60-62	37	7.3	-	89.6	89.6	2.3

TABLE 3

Addition of Hydrogen Sulfide to Phenyl Vinyl Ether

Experiment No.	Amount of H_2S (moles per mole of ether)	Experiment conditions					Unchanged ether (%)	Yield of reaction products % on ether that reacted		
		Catalyst		Duration of experiment (days)	Conditions of heating			Thiol	Sulfide	Total
		Name	Amount		Time (hours)	Temperature (°C)				
1	0.9	Traces of oxygen		70	Room		89.2	70.0	-	70
5	0.9	HCl in dioxane	0.02 ml	8	40 40	60 40	36	44.8	46.6	91.4
6	0.6	"	0.02 ml	15	122 120	60 35	39	24.6	65.1	89.7
7	2.2	Ascaidole	0.21 g	8	Room		99	-	-	-
10	2		0.2 g	5	34	60	45	75.8	15.9	91.7
8	0.9		0.2 g	16	53	60	41	40.3	47.6	87.9
9	2.1	Azonitrile	0.04 g	16	53	60	-	62.4	32.0	94.4

TABLE 4

Addition of Hydrogen Sulfide to p-tert-Butylphenyl Vinyl Ether

Experiment No.	Amount of H_2S (moles per mole of ether)	Experiment conditions					Unchanged ether (%)	Yield of reaction products, % on ether that reacted		
		Catalyst		Duration of experiment (days)	Conditions of heating			Thiol	Sulfide	Total
		Name	Amount		Time (hours)	Temperature (°C)				
3	2.1	Ascaridole	0.3	10	52	60	94.5	-	-	-
2	4.2	Azo nitrile	0.05	35	Room		55.8	26.6	70.2	96.8
1	0.9		0.05	9	52	60	7.6	19.2	73.0	92.2
5	2.1		0.03	8	55	60	-	36.3	53.5	89.8

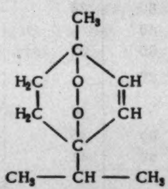
The characteristic behavior of the azo nitrile as an active radical catalyst is shown in the reaction of hydrogen sulfide with alkyl vinyl ethers, which are well known for their great tendency to combine with reagents of the type HX by an ionic mechanism. Tables 1 and 2 give comparisons of experimental material obtained for two alkyl vinyl ethers in presence of all of the catalysts that we studied. In presence of traces of oxygen and of a solution of HCl in dioxane the yield of addition products formed in accordance with Markovnikov's rule was fairly high for some alkyl vinyl ethers (for example, for cyclohexyl vinyl ether). The application of the azo nitrile enabled the extent to which the normal reaction occurred to be reduced to a minimum and was equally effective for all alkyl vinyl ethers, including cyclohexyl vinyl ether. It is probable that the azo nitrile was the most effective catalyst because it promoted rapid anomalous addition to a greater extent than other catalysts.

2,2'-Azobis[2-methylpropionitrile] can be recommended as a universal catalyst for the reaction of anomalous addition between hydrogen sulfide or a thiol and a vinyl ether of any structure.

EXPERIMENTAL

The addition of liquid hydrogen sulfide to vinyl ethers was carried out by the procedure and under the conditions that we have described in detail in previous papers [1, 2.].

Catalysts: 2,2'-Azobis[2-methylpropionitrile] was recrystallized from methanol and melted at 104°. Ascaridole



was prepared from Soviet chenopodium oil. A wide ascaridole fraction was collected (60-70% of raw material; b.p. 90-93°/7mm). After refractionation, the ascaridole was purified by a method given in the literature [12], which consisted in two crystallizations from pentane solution at −60 to −70° and distillation of the frozen-out fraction. The purified ascaridole had the following constants: b.p. 91° (7 mm), 84.5-85° (5.7 mm); n_D^{20} 1.4740. The analysis was carried out by the iodometric method described in the same paper [12]. The ascaridole content was 99.8-100.2%.

The amounts of catalyst taken were 0.2% of the azo nitrile and 1% of ascaridole on the weight of vinyl ether. In Tables 1-4 the yields are calculated on the amount of ether that reacted, not on the amount taken. The total yield does not therefore give an indication of the extent to which reaction occurred, but only of the relative amounts of products in the given experiment.

I. Addition of Hydrogen Sulfide to Aryl Vinyl Ethers

1. Phenyl Vinyl Ether and Hydrogen Sulfide. The phenyl vinyl ether was purified by the method described previously [13], and it had the following constants: b.p. 155-156° (760 mm): n_D^{20} 1.5225; d_4^{20} 0.9767.

Data relating to the experiments on the addition of hydrogen sulfide to phenyl vinyl ether in presence of various catalysts are given in Table 3. The amount of ether taken varied from 15 to 25 g. Two of the experiments are described in detail below: in one of these the catalyst was HCl in dioxane, and in the other it was 2,2'-azobis [2-methylpropionitrile].

Experiment 6 (conditions given in Table 3). The substances taken were 25 g of the ether, 4.2 g of hydrogen sulfide (0.6 mole per mole of ether), and 0.02 ml of HCl-dioxane. The tube was opened after 15 days, which included 122 hours at 60° and 120 hours at 35°. After removal of uncombined hydrogen sulfide, the increase in weight of the reaction mixture was 2.8 g. Fractionation yielded the following fractions:

Fraction I	B.p. 30-32° (4 mm); n_D^{20} 1.5210; 9.8 g
Fraction II	B.p. 94-95° (4 mm); n_D^{20} 1.5630; 4.8 g

The residue, which was completely colorless, crystallized (11.3 g).

Fraction I was unchanged phenyl vinyl ether. After refractionation, Fraction II came over entirely at 94-95° (5 mm); it was 2-phenoxyethanethiol $C_6H_5OCH_2CH_2SH$, b.p. 96-97° (4.5 mm); 106-108.5° (7.5 mm); n_D^{20} 1.5610; d_4^{20} 1.1027; found MR 45.29; calculated MR 44.88.

Found %: C 62.44 62.38; H 6.44; 6.61; S 20.60; 20.88
$C_8H_{10}OS$. Calculated %: C 62.30; H 6.54; S 20.79

When treated with alcoholic mercuric chloride, the thiol gave the mercurichloride $C_6H_5OCH_2CH_2SHgCl$, which crystallized from boiling alcohol in the form of fine threadlike crystals, the melting point of which was indefinite. It was recrystallized from boiling xylene.

Found %: C 24.58; 24.30; H 2.34; 2.49
$C_8H_9OSHgCl$. Calculated %: C 24.68; H 2.33

For 2-phenoxyethanethiol the literature gives b.p. 112° (7.5 mm) [14]; b.p. 134° (29 mm); n_D^{23} 1.5597 [15]. In the first of these investigations the thiol was synthesized by the condensation of 2-phenoxyethyl halide with hydrogen sulfide in presence of sodium ethoxide, and in the second it was obtained by a complex multistage synthesis from substances that are not readily accessible.

The crystalline sulfide fraction was distilled from a pear-shaped flask, when it came over at 181-183° (1.5-1.8 mm). After recrystallization from warm ethanol the sulfide melted at 54-55°.

Found %: C 69.96; 69.91; H 6.67; 6.80; S 11.59; 11.44
$C_{16}H_{18}O_2S$. Calculated %: C 70.04; H 6.61; S 11.66

The sulfide contained none of the isomeric monothioacetal $CH_3CH(OC_6H_5)SCH_2CH_2OC_6H_5$ as impurity, for its alcoholic solution did not give the reaction, characteristic for this class of substances, with alcoholic mercuric chloride in presence of Methyl orange [16]; it therefore consisted of bis(2-phenoxyethyl) sulfide $(C_6H_5OCH_2CH_2)_2S$. The literature gives a melting point of 54.2° for this sulfide, which was prepared by the condensation of mustard gas with sodium phenoxide [17].

Experiment 9 (conditions given in Table 3). The substances taken were 20 g of phenyl vinyl ether, 12 g of hydrogen sulfide (2.1 moles per mole of ether), and 0.04 g of 2,2'-azobis[2-methylpropionitrile]. After 16 days, which included a period of 53 hours at 60°, the tube was opened. The increase in weight was 4.2 g. No unchanged phenyl vinyl ether could be detected. Fractionation yielded 16 g of pure 2-phenoxyethanethiol, b.p. 96-100° (4-4.5 mm) and n_D^{20} 1.5600, i.e. having constants close to those already given for this substance (Experiment 6). The residue remaining after removal of the thiol fraction was transferred while hot to a tared weighing bottle, in which it crystallized (7.2 g). After a single recrystallization from warm alcohol it melted at 54.5-55°, which corresponds to bis(2-phenoxyethyl) sulfide. Thus, the use of the azo nitrile greatly increased the rate at which hydrogen sulfide added to phenyl vinyl ether.

2. p-tert-Butylphenyl Vinyl Ether and Hydrogen Sulfide. The p-tert-butylphenyl vinyl ether had b.p. 88.5-89° (6 mm); 80.5-81.5° (4.5 mm); n_D^{18} 1.5090. The experiments on the addition of hydrogen sulfide to p-tert-butylphenyl vinyl ether were carried out with 15-25 g portions of the ether; the data are given in Table 4. Only ascaridole and 2,2'-azobis[2-methylpropionitrile] were used as catalysts. It was not considered to be desirable to try less effective catalysts, since even ascaridole did not bring about the addition of hydrogen sulfide to p-tert-butylphenyl vinyl ether after a long period of heating.

Experiment 5 (conditions given in Table 4). The substances taken were 15 g of the ether, 6 g of hydrogen sulfide (2.1 moles per mole of ether), and 0.03 g of 2,2'-azobis[2-methylpropionitrile]. Vacuum fractionation of the products yielded 8 g of a substance boiling at 132-134° (4 mm). The greenish viscous liquid remaining in the distilling flask was transferred while hot to a tared weighing bottle, in which it crystallized as it slowly cooled (8 g).

Redistillation of the liquid fraction yielded:

Fraction I, b.p. 120-130-142° (7 mm); 0.5 g
Fraction II. b.p. 142-143° (7 mm); 6.5 g

The residue from this distillation (0.8 g) crystallized.

Fraction II, a colorless evil-smelling liquid, had the following constants after refractionation: b.p. 134-134.5 (4.5 mm); n_D^{20} 1.4536; d_4^{20} 1.0206; found MR 64.12; calculated MR 63.35.

Found %: C 68.63 68.45; H 8.72; 8.63; S 15.33; 15.33
$C_{12}H_{18}OS$. Calculated %: C 68.52; H 8.63; S 15.25

The substance corresponded in analysis to 2-p-tert-butylphenoxyethanethiol $C_{10}H_{13}OCH_2CH_2SH$; it was obtained in 36.3% yield.

It was converted by alcoholic mercuric chloride into its mercurichloride $C_{10}H_{13}OCH_2CH_2SHgCl$, which was recrystallized twice from boiling alcohol and then melted with decomposition at 207°.

Found %: C 32.69 32.68; H 4.03; 4.00; Cl 7.74; 7.86
$C_{12}H_{17}OSHgCl$. Calculated %: C 32.36; H 3.85; Cl 7.96

After recrystallization (twice) from very small amounts of alcohol, the crystalline sulfide fraction no longer had any odor. It melted at 43.5°.

Found %: C 74.55; 74.63; H 8.90; 8.82; S 8.48; 8.53
$C_{24}H_{34}O_2S$. Calculated %: C 74.56; H 8.87 S 8.30

The sulfide did not give the qualitative reaction for the isomeric monothioacetal, and was therefore pure bis(2-p-tert-butylphenoxyethyl) sulfide $(C_{10}H_{13}OCH_2CH_2)_2S$, obtained in 53.5% yield.

II. Addition of Hydrogen Sulfide to Alkyl Vinyl Ethers

Tables 1 and 2 give comparisons of the results of experiments on the addition of hydrogen sulfide to butyl and cyclohexyl vinyl ethers in presence of various catalysts. Below, we describe one experiment for each ether in presence of the most effective catalyst -2,2'-azobis[2-methylpropionitrile].

1. Butyl Vinyl Ether and Hydrogen Sulfide. Experiment 94 (conditions given in Table 1). In the fractionation 7.4 g of unchanged butyl vinyl ether was obtained and also

Fraction I b.p. 40-44° (4 mm), n_D^{20} 1.4489; 4 g
Fraction II b.p. to 125° (3.5 mm); 0.3 g
Fraction III b.p. 125-127° (3.5 mm); n_D^{20} 1.4559; 11 g

Fraction I corresponded in constants to 2-butoxyethanethiol, which we have previously characterized [1]. It was obtained in 23.8% yield, and its mercurichloride had m.p. 137.5-138°, undepressed by admixture of the mercurichloride of 2-butoxyethanethiol obtained previously. Fraction III corresponded in constants with bis(2-butoxyethanethiol obtained previously. Fraction III corresponded in constants with bis(2-butoxyethyl)sulfide $(C_4H_9OCH_2CH_2)_2S$. which we have characterized previously. It was obtained in 74.5% yield.

2. Cyclohexyl Vinyl Ether and Hydrogen Sulfide. Experiment 11 (conditions given in Table 2). The whole of the cyclohexyl vinyl ether reacted. Fractionation of the reaction mixture yielded

Fraction I b.p. 78-80° (5 mm); n_D^{20} 1.4865; 5.5 g
Fraction II b.p. 183-185° (5 mm); n_D^{20} 1.4988; 11.5 g

Fraction I was pure 2-cyclohexyloxyethanethiol, the constants of which were close to those given previously [2] for this substance; it was obtained in 28.9% yield. Fraction II was almost pure bis(2-cyclohexyloxyethyl) sulfide, and was identical in constants with the sulfide that we prepared previously [2]; it was obtained in 67.5% yield.

SUMMARY

1. The reaction conditions required for the anomalous addition of hydrogen sulfide to aryl vinyl ethers were studied. It was shown that, while the general tendency of aryl vinyl ethers is to react more slowly than alkyl vinyl ethers, the addition of hydrogen sulfide to the former proceeds entirely in the direction contrary to that required by Markovnikov's rule.

2. A simple method is proposed for the synthesis in quantitative yield of 2-aryloxyethanethiols and bis (2-aryloxyethyl) sulfides.

3. It was shown that the most effective radical catalyst for anomalous addition of hydrogen sulfide to vinyl ethers of any structure is 2,2'-azobis[2-methylpropionitrile].

Received September 16, 1954

N. D. Zelinsky Institute of Organic Chemistry of
the USSR Academy of Sciences

LITERATURE CITED

[1] M. F. Shostakovsky, E. N. Prilezhaeva, and E. S. Shapiro, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No. 2, 292, (T.p. 235)*.

[2] M. F. Shostakovsky, E. N. Prilezhaeva, and E. S. Shapiro, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No. 2, 303, (T.p. 245)*.

[3] M. F. Shostakovsky and A. V. Bogdanova, J. Gen. Chem. 21, 632, (1951), (T.p. 697)*.

[4] M. F. Shostakovsky and A. V. Bogdanova, J. Gen. Chem. 20, 1326 (1950), (T.p. 1379)*.

[5] M. F. Shostakovsky and A. V. Bogdanova, J. Gen. Chem. 21, 394, (1951), (T.p. 435)*, 21, 388 (1951), (T.p. 489)*.

[6] M. F. Shostakovsky and A. V. Bogdanova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No. 5, 911 (T.p. 789)*.

[7] I. P. Losev, O. Ya. Fedotova, and E. B. Trostyanskaya, J. Gen. Chem. 15, 353 (1935).

[8] M. F. Shostakovsky and A. V. Bogdanova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No. 5, 919, (T.p. 797)*.

[9] M. F. Shostakovsky, in the Collection "Problems of the Mechanism of Organic Reactions", Acad. Sci. UkrSSR Press, Kiev, 1954, p. 175.

[10] U. S. Patent 2531602; C.A. 1952, 4372.

[11] C. G. Oberberger, M. T. O'Shaugnessy and H. Shalit, J. Am. Chem. Soc. 71, 2661 (1949).

[12] H. Böhme and K. Ernster, Arch. d. Pharm. 248/56, 971 (1951.

[13] M. F. Shostakovsky and E. N. Prilezhaeva, J. Gen. Chem. 17, 1129 (1947).

[14] G. L. Brauning, Jr., U. S. Patent 2460567; C. A. 43, 4507 (1949).

[15] I. H. Chapman and L. N. Owen, Soc. 579 (1950)**.

[16] E. N. Prilezhaeva, E. S. Shapiro, and M. F. Shostakovsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1951, No. 4, 438.

[17] O. B. Helfrich, E. E. Reid, J. Am. Chem. Soc. 42, 1208 (1920).

---

* T.p. = C. B. Translation pagination.

** Reference as given in original.

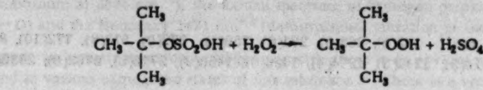
BLANK
PAGE

SYNTHESIS OF tert-BUTYL HYDROPEROXIDE AND tert-BUTYL PEROXIDE AND THEIR OPTICAL INVESTIGATION IN RELATION TO THE PROBLEM OF THE STRUCTURE OF HYDROGEN PEROXIDE

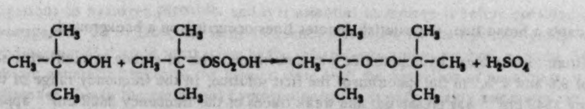
A. P. Meshcheryakov, M. I. Batuev, and A. D. Matveeva

As is well known, many peroxides are unstable compounds, which may explore violently [1]; these include, in particular, peroxides derived from dienes and acetylenic compounds. However, some very stable peroxides are known – stable not only at ordinary, but also at high temperatures. Such peroxides are those derived from tertiary alcohols, namely, tert-butyl alcohol and higher alcohols of this type.

In 1938 Milas and coworkers [2] prepared tert-butyl hydroperoxide and tert-butyl peroxide, which have found application, along with other peroxides, in polymerization processes [3, 4]. For the preparation of these peroxy compounds we alkylated hydrogen peroxide with tert-butyl hydrogen sulfate:



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OSO_2OH + H_2O_2 \rightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OOH + H_2SO_4;$$



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OOH + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OSO_2OH \rightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-O-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 + H_2SO_4$$

Whereas Milas and coworkers prepared tert-butyl hydrogen sulfate from tert-butyl alcohol, we prepared from a more accessible substance, isobutene, which can be obtained from isobutyl alcohol by dehydration over alumina at 400-420°, or from cracking gases.

EXPERIMENTAL *

We prepared tert-butyl hydrogen sulfate by the absorption of isobutene in 63% sulfuric acid at 0-20°. The resulting mixture of tert-butyl hydrogen sulfate and sulfuric acid was transferred to a Grignard-reaction flask and was cooled to 0°. Hydrogen peroxide (27%) was then added gradually at 0-10° from a dropping funnel over a period of 30-60 minutes, the amount added being one mole for every two moles of tert-butyl hydrogen sulfate. Stirring was continued for 4-5 hours, and the mixture was then left at room temperature overnight. As a result of the reaction a completely transparent layer consisting of a mixture of peroxide and hydroperoxide was formed. This mixture can be used for various purposes – in particular, for polymerizations, and for the synthesis of peroxybenzoates and other peroxy compounds [2].

In order to prepare pure tert-butyl peroxide, free from hydroperoxide, the mixture was separated from sulfuric acid in a separating funnel and treated in the same Grignard flask at 0-10° with 10-20% NaOH solution**, which resulted in the formation of the sodium salt of the hydroperoxide and the isolation of pure (almost 100% pure) tert butyl peroxide, which was washed three times with small amounts of water and dried over sodium sulfate. The hydroperoxide was isolated by treating the sodium salt at 0-15° with 10% sulfuric acid, extracting the solution with ether, drying the ether solution over sodium sulfate, distilling off ether, and vacuum-distilling the residue at 35-37° (17 mm).

The total yield of peroxide and hydroperoxide was greater than 80%. When 2.1-2.2 moles of tert-butyl hydrogen sulfate were taken for every one mole of hydrogen peroxide, then after a long treatment (stirring for 8-10 hours) the main product was tert-butyl peroxide. Thus, 575 g of a mixture of 63% sulfuric acid and tert-butyl hydrogen sulfate (1.1 moles) reacting with 63 g of 27% hydrogen peroxide (16.81 g of H_2O_2) yielded 67.2 g of tert-butyl peroxide, which is 81.8% of the theoretically possible yield.

---

* Laboratory worker A. E. Korolkova took part in the experimental work.

** During the treatment with NaOH solution there was a transient purple coloration.

Physicochemical Constants and Analytical Results

1. tert-Butyl Hydroperoxide: b.p. 35-37° (17 mm); M 90.12; d_4^{20} 0.8960; n_D^{20} 1.4015. The literature gives d_4^{20} 0.896; n_D^{20} 1.4013.

Found %: C 52.83; H 11.0; 11.03
$C_4H_{10}O_2$. Calculated %: C 53.3; H 11.18

2. tert-Butyl Peroxide: b.p. 13-15° (20 mm); M 146.224 d_4^{20} 0.7970; n_D^{20} 1.3910.

Found %: C 66.18; 66.20; H 12.45; 12.69
$C_8H_{18}O_2$. Calculated %: C 65.77; H 12.40

The somewhat high carbon content of the peroxide is probably to be explained by the presence of a small amount of higher peroxides.

We investigated the Raman spectra of tert-butyl hydroperoxide and tert-butyl peroxide; the spectrum data are given below. The spectra were determined on a Soviet ISP-51 spectrograph with the medium camera.

$(CH_3)_3COOH$. $\Delta\nu$ cm^{-1}: 221(1), 270(1), 346(4), 365(4) 413(1), 527(5), 562(0), 589(0), 609(0), 628(0), 670(0), 749(10), 790(0), 846(5), 884(10), 920(5), 1027(4), 1063(0), 1194(4), 1252(6b), 1424(0), 1454(10), 1471(2), 2655(0), 2721(1), 2884(4*), 2931(10*), 2987(10*), 3236(3 band), 3320-3500(3band with maximum at 3403), 3546(1).

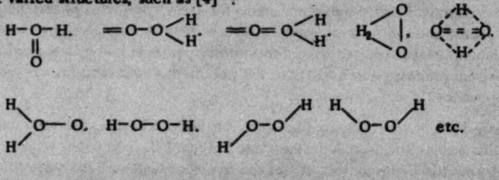
$(CH_3)_3C-O-O-C(CH_3)_3$. $\Delta\nu$ cm^{-1}: 245(5), 263(0), 291(6), 350(2), 372(0), 513(8), 772(10), 862(10), 904(0), 928(3), 1022(3), 1041(3), 1210(3), 1241(3), 1274(4), 1426(0), 1453(9), 2712(2), 2762(0), 2882(4*), 2930 (10*), 2986(10*).

NOTE: b indicates a broad line; the asterisk denotes lines occurring on a background.

The Raman spectrum of tert-butyl hydroperoxide was determined also in carbon tetrachloride solution at molar concentrations of 9.6 and 4 %. In the spectrum of the first solution, in the frequency range of the hydroxyl group only the frequency 3546 cm^{-1} was preserved, and weak traces of the frequency 3622 cm^{-1} appeared. In the spectrum of the second solution, the intensity of the latter frequency was much higher, while the frequency 3546 cm^{-1} was preserved at fairly high intensity (the ratio of the intensities of the frequencies 3546 and 3622 cm^{-1} was 3 : 1).

The investigated hydroperoxide can be regarded as a derivative of hydrogen peroxide in which one of the hydrogens has been replaced by the group $C(CH_3)_3$. It is to be expected, therefore, that the hydroperoxide will retain some of the main optical characteristics of hydrogen peroxide.

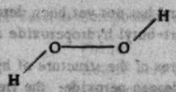
In the course of chemical and physicochemical investigations on hydrogen peroxide, this compound has been assigned the most varied structures, such as [4] *:



Optical investigations of the last two or three decades have directly established the presence of the linkages −O−O− and O−H and the absence of the linkage O=O in the hydrogen peroxide molecule. Hence, many of the proposed structural formulas for hydrogen peroxide containing ter- and quadri-valent oxygen, etc., have automatically dropped out. The reults of the optical investigation of hydrogen peroxide, taken in conjunction with the fact that its dipole moment is so high ($2 \cdot 13 \cdot 10^{-18}$ in dioxane and $2.06 \cdot 10^{-18}$ in ether) and with the established absence of free rotation around the axis −O−O−, have led to the now generally accepted view of the nonplanar structure of the hydrogen peroxide molecule: the linkage O−H forms an angle of about 110° to the −O−O− axis, and H−O−O and O−O−H are in mutually perpendicular planes [4, 5].

---

* The broken lines represent partial valencies and the arrow represents a coordinate semipolar covalent link.



Various physicochemical data indicate that hydrogen peroxide is an associated liquid, and the available Raman spectrum data [6] show directly that this association is the result of hydrogen bonding (in alcohol the hydroxyl frequency is represented not by a line, but by a band having a maximum at 3395 cm^{-1}). The degree of association at 0°, determined by the formula of Ramsay and Shields, has been given as 3.48 [7]. The density of hydrogen peroxide is very much greater than those of water and organic hydroperoxides [1], as can be seen from the data cited.

Peroxy compound	Temperature (°C)	Density (g/cc)
H−O−O−H.	22	1,4403
CH_3−O−O−H	15	0.9967
C_2H_5−O−O−H.	15	0.9550
CH_3CH_2−O−O−CH_2−OH	16	1.0453

This last fact indicates the particularly close packing of hydrogen peroxide molecules brought about by the action of hydrogen bonds. It is interesting to note that the addition of water sharply reduces the density of hydrogen peroxide [8]; water molecules, by forming hydrogen bonds with hydrogen peroxide molecules, break down the specific close packing with consequent reduction in the density.

Apart from the hydroxyl frequencies referred to above (band with maximum at 3395 cm^{-1}), the Raman spectrum of hydrogen peroxide contains the frequency 887 cm^{-1} (vibration of O−O) and the frequency 1421 cm^{-1} (deformational vibration of the linkage O−H) [5, 9].

However, in investigations on hydrogen peroxide there is an obvious underestimation of the part played by the hydrogen bond in various aggregated states of this substance.* There is a very notable obscurity in the results of optical investigations on hydrogen peroxide, and it is essential to remove it before considering the hydroperoxide that we have investigated. Up to 1950, the same frequency was found for the hydroxyl group of hydrogen peroxide in both the liquid and gaseous (60° at 18 mm) states by the infrared-absorption method, namely, 3418 cm^{-1} [5, 10]. As hydrogen bonds are generally broken in the gaseous state with the formation of monomers, it was concluded [5] that in the liquid phase (as also in the gas phase) hydrogen peroxide is only weakly associated, so that individual molecules of the liquid will be characterized by the same hydroxyl frequency as the monomeric molecules of the gas phase. In view of the statements that we have made above concerning the association of hydrogen peroxide molecules by hydrogen bonding and the resulting very dense packing of molecules into associated complexes, the data cited on the identity of hydroxyl frequencies (a band with a maximum at 3418 cm^{-1}) show definitely that under these experimental conditions the frequency of the hydroxyl of hydrogen-bonded associated complexes is observed even in gaseous hydrogen peroxide. Indeed, under these experimental conditions, the frequency of the hydroxyl of isolated hydrogen peroxide molecules was not observed; it must undoubtedly lie at a higher frequency than 3400 cm^{-1}. This view is supported by the following data: hydrogen peroxide has an appreciable acid dissociation constant (into H^+ and OOH^-); it has been estimated [4] at $1.78 \cdot 10^{-12}$ (Evans) and $1.55 \cdot 10^{-12}$ (Kargin). It is considerably higher than the dissociation constant of aliphatic alcohols (e.g. methanol, $1 \cdot 10^{-16}$), but it is less than the constant for phenol ($1.06 \cdot 10^{-10}$), and of course very much less than the constants of formic ($2.1 \cdot 10^{-4}$) and acetic ($1.8 \cdot 10^{-5}$) acids. The frequency of the hydroxyl of the monomeric hydrogen peroxide molecule should therefore be greater than in formic acid (3563 cm^{-1}) and phenol (3603 cm^{-1}), but less than in methanol (3670 cm^{-1}) [12].

In this connection it must be noted that in a recent investigation reported in 1950 [13] a band at 3590 cm^{-1} was observed in the infrared spectrum of gaseous hydrogen peroxide under more severe conditions (90° and 15 mm) while the frequency of 3400 cm^{-1}, observed earlier [5, 10] under somewhat milder conditions (60° and 18 mm) in the gas phase and also in the liquid phase, could not be detected under these conditions. The author [13], without even considering the question of the association of hydrogen peroxide molecules by hydrogen bonding, of the dependence of this association on the experimental conditions, and of the effect of all these circumstances on the spectrum of the hydroxyl group, provisionally, but without any basis, assigned the frequency of 3400 cm^{-1} to the symmetrical, and the frequency of 3590 cm^{-1} to the antisymmetrical, vibration of the hydroxyls of the isolated hydrogen peroxide molecule. It will be evident, however, from the consideration given above that the frequency 3400 cm^{-1} (which is in the form of a broad band in the Raman spectrum) can in no circumstances be assigned to the hydroxyl of the isolated hydrogen peroxide molecule. Its replacement by the frequency 3590 cm^{-1} in gaseous hydrogen peroxide at a somewhat higher temperature (90° instead of 60°) undoubtedly indicates that under these conditions the associated complexes are broken down into simpler ones, but it is very unlikely that the frequency 3590 cm^{-1} is that of the hydroxyl of the monomeric molecule; it is probable that it is the frequency of a hydroxyl forming a part of the dimer ring, which is not broken down under the experimental conditions**, the frequency of the hydroxyl of the monomeric hydrogen peroxide molecule is still higher and has not yet been detected. Apart from the physicochemical data cited, the results of our optical investigations on tert-butyl hydroperoxide also support this view.

---

* By way of example we may point out that in Pozin's monograph [4], in which a large amount of material is gathered together from the literature, there is no mention of the presence of a hydrogen bond in hydrogen peroxide; the same is true of Rieche's book [1].

** See following page.

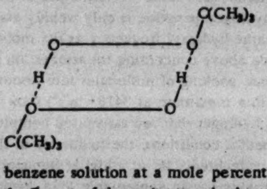
In this hydroperoxide the main features of the structure of hydrogen peroxide are retained. The frequencies observed vary only slightly from those of hydrogen peroxide: the frequency of the vibration of the O—O group is 884 cm^{-1} (877 for hydrogen peroxide), the frequency of the deformational vibration of the hydroxyl group is 1424 cm^{-1} (1421 for hydrogen peroxide), and there is a hydroxyl band with its maximum at 3403 cm^{-1} (3395 for hydrogen peroxide), i.e., in the investigated hydroperoxide in the liquid state, association occurs by hydrogen bonding (the hydroxyl frequency is displaced toward the lower frequencies and is smeared into a band). But apart from this band, in the region of the hydroxyl frequencies there is a frequency of 3546 cm^{-1}, which is preserved also in the spectra of the 9.6 % and 4% solutions of the hydroperoxide in carbon tetrachloride, in which the other frequencies of this region disappear and a new frequency of 3622 cm^{-1} makes its appearance – faintly in the spectrum of the first solution, and as a more intense line in the spectrum of the second. This is a new phenomenon, not to be found in the results given above for hydrogen peroxide. We shall explain the signifiance of this phenomenon.

As our cryoscopic investigations showed, the hydroperoxide is a substance that is associated by hydrogen bonding. At a 4 mole-% concentration in benzene solution the association coefficient of the hydroperoxide is 1.48, i.e., by no means all of the hydrogen-bonded associated complexes are broken down into monomer at this concentration. At a concentration in benzene solution of 8–10 mole-% there is a very definite predominance of dimer, and with increase in concentration the association coefficient increases still further.

Cryoscopic Determination of the Molecular Weight of tert-Butyl Hydroperoxide in Benzene

Concentration of solution (mole-%):	4	7.8	8.4	16.8	32.9
Association coefficient:	1.48	1.88	1.94	4.02	8.57

Since, unlike hydrogen peroxide, it has only one hydroxyl group, the investigated hydroperoxide forms simpler associated complexes, and its main association unit, unlike that of hydrogen peroxide with its two hydroxyls (see above), is a planar dimer ring:



tert-Butyl hydroperoxide in benzene solution at a mole percentage of 8–10 exists almost entirely in the form of this dimer ring, but at 4 mole-% part of these rings are broken with the formation of monomeric molecules. On the other hand, at higher concentrations and in the liquid state further association occurs into complexes formed from many molecules, resulting, in particular, by the further hydrogen bonding of the already existing dimer rings in layer fashion.

In the light of these considerations, the results that we have discussed relating to the optical investigation of the hydroxyl region of the spectrum are fully comprehensible. The frequency 3546 cm^{-1}, which is present in the spectrum of the 9.6 and 4 mole-% solutions of the hydroperoxide in carbon tetrachloride, is to be assigned (in accordance with the cryoscopic data cited above) to the hydroxyl group of the dimer ring shown above, in which the association occurs through two hydrogen bonds. The fact that this frequency is lower than that of the hydroxyl of isolated formic and acetic acid molecules (in the gas phase [12]) provides particularly strong support for the view that under these conditions we are indeed concerned with the frequency of a hydroxyl that is taking part in a hydrogen bond, and not with the frequency of the hydroxyl in an isolated molecule. The higher frequency of 3622 cm^{-1} characterizes the vibrations of the hydroxyl of monomeric molecules, which in the first solution are present only in traces (judging from the cryoscopic data), but in the second are present to the extent of about one in five of all the hydroperoxide molecules present in the solution. The presence in the liquid hydroperoxide of the frequency 3546 cm^{-1} in addition to the band indicates that in the liquid state dimer rings are able to exist in appreciable amount along with the polymeric complexes.

The frequency of the hydroxyl group of the monomeric molecule of the investigated hydroperoxide is higher than the hydroxyl frequency of monomeric fatty acids (formic, etc.) and phenols, but lower than that of trimethylsilanol, methanol, and other substances, which is in accord with the discussion given above of the degree of acidity of these compounds [12, 14].

•• As is well known, complete breakdown of the hydrogen-bonded dimer ring of acetic acid occurs only at 200° (the boiling point of acetic acid is 118.1°).

Hydroxyl Frequency of Monomeric Molecules of Various Compounds (cm^{-1})

OH$^-$ ion	4200	Phenol	3603
Trimethylsilanol	3702	Acetic acid	3578
Methanol	3683	Formic acid	3563
tert-Butyl hydroperoxide	3620	·OH radical	3480

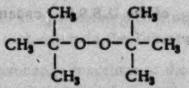
In accordance with our discussion above the frequency of the hydroxyl of the monomeric molecule of hydrogen peroxide should also be found in the Raman spectrum in the region of 3622 cm^{-1} (symmetrical vibration) and in the infrared spectrum (antisymmetrical vibration) at a somewhat higher frequency. If we regard the frequency 3590 cm^{-1} in the infrared absorption spectrum as the frequency of antisymmetrical vibrations of the hydroxyls of the dimer ring of hydrogen peroxide, then in the hydrogen peroxide Raman spectrum the vibration frequency of these hydroxyls (symmetrical vibration) should be somewhat lower.

Let us now turn to the question of the extent to which the optical manifestation of a quaternary carbon atom at one or other end of a carbon chain is preserved in the investigated hydroperoxide and peroxide, in which one of the C−C bonds of the quaternary carbon atom is replaced by a C−O atom.

The presence of a quaternary carbon atom at the end of the chain of a hydrocarbon molecule is characterized by a set of fairly intensive lines − 746, 926, 1207, 1250 cm^{-1} [15]. The spectrum of the investigated hydroperoxide contains the frequencies 749, (10), 920(5), 1194(4), 1252(6b). As will be seen, the replacement of one of the C−C bonds of the quaternary atom by C−O, does not produce any essential change in the set of frequencies characteristic of this branching. In tert-butyl peroxide this set of frequencies is again largely preserved with some of them slightly higher: 772(10), 926(3), 1210(3), and the fourth split into two, 1241(3) and 1274(4). The O−O frequency in tert-butyl hydroperoxide is close to that of hydrogen peroxide (884 and 877 cm^{-1}, respectively), and in tert-butyl peroxide it is split into two, 862 and 904 cm^{-1}.

The high symmetry of the tert-butyl peroxide molecule, as compared with the tert-butyl hydroperoxide molecule, results in a great simplification of the spectrum (the appearance of a large number of degenerate vibrations): whereas in the Raman spectrum of tert-butyl hydroperoxide 31 vibrations were observed out of a possible 42 (for 16 atoms in the molecule), of the 78 possible vibrations of the tert-butyl peroxide molecule (18 atoms in the molecule) only 22 were observed.

Unlike other alkyl peroxides, tert-butyl peroxide has two quaternary carbon atoms in its molecule:



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-O-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3$$

and it is for this reason that it is so very stable, for in its molecule the carbons adjacent to the oxygens are not attached to hydrogen and do not carry double or triple bonds, so that under ordinary conditions (room temperature) a chain oxidation reaction (which in other peroxides often occurs, leading to violent decomposition and explosions) cannot readily occur.

SUMMARY

1. It is shown that tert-butyl hydroperoxide and tert-butyl peroxide can be prepared from isobutene.

2. It is shown that in previous investigations insufficient account has been taken of the part played by hydrogen bonding in hydrogen peroxide, of which tert-butyl hydroperoxide is a derivative (a fact that is amply confirmed by the presence in the Raman spectrum of the frequencies associated with all of the analogous vibrations of the molecules of the two substances). A study of the Raman spectrum of tert-butyl hydroperoxide shows that hydrogen bonding occurs in this substance. The optical characteritistics of the hydroxyl group have been found for complexes formed from many molecules associated through hydrogen bonds (band with a maximum at 3403 cm^{-1}), for the dimer ring (line at 3456 cm^{-1}), and for the monomeric molecule (line at 3622 cm^{-1}). This optical characterization was confirmed by a cryoscopic investigation. The degree of acidity of tert-butyl hydroperoxide was determined optically. It was shown that the optical characteristics of quaternary branching at the ends of the chains of tert-butyl hydroperoxide, tert-butyl peroxide, and the corresponding hydrocarbons were almost identical.

3. The stability of the investigated peroxide is explained by its structural characteristics.

LITERATURE CITED

[1] A. Rieche, Alkylperoxide und Ozonide, Dresden, Leipzig, 1931.

[2] N. A. Milas, S. A Herris, J. Am. Chem. Soc., 60, 2434 (1938); N. A. Milas, M. Surgenor, ibid, 68, 205 (1946); 68, 642, (1946); 68, 643 (1946); N. A. Milas, L. Perry, ibid, 68, 1938 (1946).

[3] R. P. Perry, K. P. Seltzer, Modern Plastics 25, 134, 216 (1947).

[4] M. E Pozin, Hydrogen Peroxide and Peroxy Compounds, State Chem. Press, 1951.

[5] K. Kohlrausch, Raman Spectra, Foreign Lit. Press, Moscow, 1952, p. 95.

[6] Ibid, p. 190.

[7] O. Maass, W. Hatcher, J. Am. Chem. Soc., 42, 2548 (1920).

[8] A. Rieche, Alkylperoxyde und Ozonide, Dresden, Leipzig, 1931, 94.

[9] F. Feher, Ber. 72, 1778 (1939).

[10] C. Baily, R. Gordon, Trans. Faraday Soc. 34, 1133 (1938).

[11] A. I. Shatenshtein, Theory of Acids and Bases, State Chem. Press, 1949, p. 127.

[12] M. I. Batuev, J. Phys. Chem. 23, 1405 (1949); Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. 1950, No. 4, 402; Div. Chem. Sci. 20, 318 (1950); M. I. Batuev, A. P. Meshcheryakov, and A. D. Matveeva, J. Expt. Theor. Phys. 20, 318 (1950); M. I. Batuev and A. D. Matveeva, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. 1951, No. 4, 448.

[13] P. Giguere, J. Chem. Phys. 18, 88 (1950).

[14] M. I. Batuev, M. F. Shostakovsky, V. L Belyaev, A. D. Matveeva, and E. V. Dubrova, Proc. Acad. Sci. U.S.S.R. 95, 531 (1954).

[15] B. I. Stepanov, J. Phys. Chem. 20, 917 (1946).

Received July 22, 1954

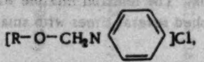
N. D. Zelinsky Institute of Organic Chemistry
of the U.S.S.R. Academy of Sciences

EXCHANGE AND CLEAVAGE REACTIONS OF QUATERNARY AMMONIUM SALTS

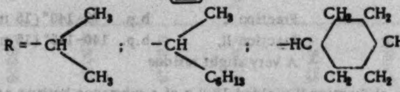
COMMUNICATION 9. REACTION OF QUATERNARY AMMONIUM SALTS OF THE TYPE $[R-O-CH_2-\overset{|}{\underset{|}{N}}-]X$ WITH SECONDARY AND TERTIARY ALCOHOLS

V. N. Setkina, N. K. Baranetskaya, and D. N Kursanov

We have shown previously [1, 2] that quaternary ammonium salts containing an alkoxymethyl group readily undergo exchange reactions in which the alkoxymethyl group changes places with the hydrogen of the hydroxyl group of a primary alcohol. The reaction has been extended to phenols [3], carboxylic acids and their salts [4], ethers [5], and esters [6]. It was of interest to determine whether the exchange reaction could be extended also to secondary and tertiary alcohols. We found no data on this in the literature. It was thought that the tendency of secondary, and particularly tertiary, alcohols to undergo dehydration might result in a change in the main direction of reaction. In our investigation of the reactions of quaternary ammonium salts with secondary and tertiary alcohols, we have used 1-(alkoxymethyl)pyridinium salts:



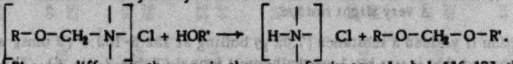
in which



These salts were prepared by the condensation of the chloromethyl ethers of secondary alcohols with pyridine. The chloromethyl ethers were prepared by a previously described method [7-10], and the constants of our products are given in Table 1.

We were not successful in synthesizing chloromethyl ethers of tertiary alcohols, and we were unable to find evidence of the existence of such ethers in the literature.

We investigated the exchange reactions of the quaternary ammonium salts with isopropyl alcohol, sec-butyl alcohol, cyclohexanol, 2-octanol, tert-butyl alcohol, and 2-methyl-2-butanol. Equimolecular amounts of the quaternary salt and the alcohol were heated at 100-120° for 10-16 hours. It was found that the reaction products were formals, so that, as in the case of the primary alcohols, the hydroxyl hydrogen of secondary and tertiary alcohols changes places with the alkoxymethyl radical in accordance with the scheme:



$$\left[R-O-CH_2-\overset{|}{\underset{|}{N}}-\right]Cl + HOR' \longrightarrow \left[H-\overset{|}{\underset{|}{N}}-\right]Cl + R-O-CH_2-O-R'.$$

When R and R' were different, then, as in the case of primary alcohols [16-18], the unsymmetrical formals underwent symmetrization, and all three possible formals were found among the reaction products:

$$2R-O-CH_2O-R' \longrightarrow R-O-CH_2-O-R + R'-O-CH_2-OR'.$$

It should be noted that the yield of formals obtained from secondary and tertiary alcohols did not exceed 50-60%, whereas primary alcohols gave formals in almost theoretical yield.

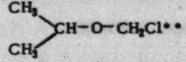
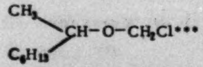
Table 2 gives the constants of formals containing tertiary and secondary radicals which we have prepared by the exchange reaction.

EXPERIMENTAL

Reaction of 1-(Alkoxymethyl)pyridinium Salts with Secondary and Tertiary Alcohols

The procedure used in the preparation of 1-(alkoxymethyl)pyridinium salts has been described previously [10].

TABLE 1

No.	Formula	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	Molecular refraction		Cl content (%)	
					Found	Calc'd	Found	Calc'd
1	$C_6H_{11}O{-}CH_2{-}Cl$•	72.2 - 72.8° (12)	1.0558	1.4678	39.12	38.84	23.66	23.86
2	 $(CH_3)_2CH{-}O{-}CH_2Cl$••	27.7 - 28.0 (45)	0.9742	1.4074	27.46	27.18	32.28	32.66
3	 $CH_3(C_6H_{13})CH{-}O{-}CH_2Cl$•••	98 - 99 (18)	0.9246	1.4357	50.50	50.27	19.60	19.84

• Data in the literature: b.p. 75° (13-14 mm) [11]; b.p. 183-185°. d_4^0 1.0712; d_4^{20} 1.0432; n_D^9 1.4713 [12].

•• Data in the literature: b.p. 98-100° [13]; b.p. 101-102° (760 mm); d_0^{20} 0.972 [14]; b.p. 97-98°; d_4^{20} 0.9790; n^{16} 1.4592 [12]; b.p. 36° (45 mm); 101° (750 mm); d_4^{20} 0.9843; n_D^{20} 1.4095 [15].

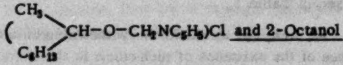
••• Chloromethyl 1-methylheptyl ether is here described for the first time.

1. 1-(Cyclohexyloxymethyl)pyridinium Chloride $(C_6H_{11}OCH_2NC_5H_5)Cl$ and Cyclohexanol $C_6H_{11}OH$. A mixture of 30.64 g (0.135 mole) of 1-(cyclohexyloxymethyl) pyridinium chloride and 13.47 g (0.135 mole) of cyclohexanol was heated at 100° for six hours under reflux. The reaction mixture was cooled and treated with water, and the upper, water-insoluble layer was separated, washed several times with small amounts of water, and dried with calcium chloride. Fractionation yielded:

Fraction I,	b.p. 72-140° (15 mm); 0.6 g
Fraction II,	b.p. 140-145° (15 mm); 19.47 g

A very slight residue

Two further distillations of Fraction II yielded 18.0 g of a substance boiling at 135.0 - 135.5° (11 mm). Its constants and analysis (Table 2, No. 1) show that this substance was pure dicyclohexyl formal. The yield was 63.0% Data in the literature: 279-280° (760 mm); d_0^{24} 0.9716; n_D 1.470; [19]; b.p. 139-140° (14 mm); d^{21} 0.9741; n_D^{21} 1.4702 [11].

2. 1-(1-Methylheptyloxymethyl)pyridinium Chloride  $(CH_3(C_6H_{13})CH{-}O{-}CH_2NC_5H_5)Cl$ and 2-Octanol $CH_3{-}CHOH{-}C_6H_{13}$. A mixture of 14.42 g (0.056 mole) of 1-(1-methylheptyloxymethyl)pyridinium chloride and 7.29 g (0.056 mole) of 2-octanol was heated at 110° for 16 hours and then treated as in the preceding experiment. Fractional distillation yielded:

Fraction I,	b.p. 58-149° (8 mm); 2.39 g
Fraction II,	b.p. 149-155° (8 mm); 7.88 g

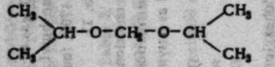
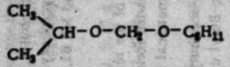
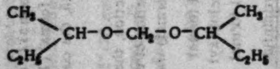
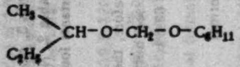
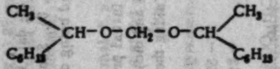
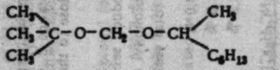
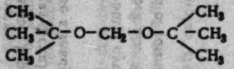
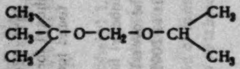
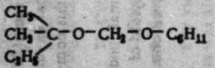
A very slight residue

Further distillation of Fraction II yielded a substance (7.02 g) boiling at 152.5-153.0° (9 mm), and its molecular refraction and analysis showed that it was bis(1-methylheptyl) formal (Table 2, No. 6). The yield was 46.0%. Data in the literature: b.p. 175-177° (16 mm); d_4^{20} 0.8499 [20].

3. 1-(Cyclohexyloxymethyl)pyridinium Chloride $(C_6H_{11}OCH_2NC_5H_5)Cl$ and sec-Butyl Alcohol $CH_3CHOH{-}CH_2{-}CH_3$. A mixture of 76.81 g (0.34 mole) of 1-(cyclohexyloxymethyl)pyridinium chloride and 25 g (0.34 mole) of sec-butyl alcohol was heated at 120-125° for 12 hours. The reaction products were treated as in the preceding experiments. Fractional distillation yielded:

Fraction I,	b.p. 60-70° (20 mm); 11.48 g
Fraction II,	b.p. 70-100° (20 mm); 0.93 g
Fraction III,	b.p. 100-115° (20 mm); 22.71 g
Fraction IV,	b.p. 115-148° (20 mm); 0.80 g
Fraction V,	b.p. 148-152° (20 mm); 9.35 g

TABLE 2

No.	Formula of formal	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	Molecular refraction		Analysis			
							C (%)		H (%)	
					Found	Calc'd	Found	Calc'd	Found	Calc'd
1	$C_6H_{11}OCH_2OC_6H_{11}$	135.0-135.5 (11)	0.9692	1.4703	61.15	61.12	73.67 73.64	73.53	11.48 11.43	11.40
2	 $(CH_3)_2CH-O-CH_2-O-CH(CH_3)_2$	55.5-56.0 (81)	0.8179	1.3842	37.80	37.81	63.40 63.45	63.59	12.05 12.19	12.20
3*	 $(CH_3)_2CH-O-CH_2-O-C_6H_{11}$	70.0-70.5 (6)	0.9089	1.4370	49.65	49.47	69.95 70.07	69.72	11.68 11.87	11.73
4	 $CH_3(C_2H_5)CH-O-CH_2-O-CH(CH_3)C_2H_5$	60.5-60.8 (17)	0.8472	1.4124	47.10	47.05	67.52 67.67	67.46	12.34 12.30	12.58
5*	 $CH_3(C_2H_5)CH-O-CH_2-O-C_6H_{11}$	99.5-101.0 (15)	0.9076	1.4402	54.10	54.08	70.43 70.64	70.85	11.93 11.73	11.91
6	 $CH_3(C_6H_{13})CH-O-CH_2-O-CH(CH_3)C_6H_{13}$	152.5-153.0 (9)	0.8419	1.4322	83.96	83.99	75.04 75.18	74.94	13.44 13.45	13.32
7*	 $(CH_3)_3C-O-CH_2-O-CH(CH_3)C_6H_{13}$	128 -129 (29)	0.8351	1.4204	65.62	65.52	72.14 72.22	72.16	13.18 13.40	13.05
8	 $(CH_3)_3C-O-CH_2-O-C(CH_3)_3$	77.0-79.5 (96)	0.8306	1.3982	46.60	47.05	67.29 67.38	67.45	12.71 12.58	12.58
9*	 $(CH_3)_3C-O-CH_2-O-CH(CH_3)_2$	71.1-71.5 (96)	0.8223	1.3930	42.44	42.43	65.53 65.45	65.70	12.29 12.24	12.41
10*	 $(CH_3)_2(C_2H_5)C-O-CH_2-O-C_6H_{11}$	119.5-120.5 (23)	0.9103	1.4453	58.60	58.70	71.54 71.32	71.45	12.11 11.98	12.08

* Formals prepared for the first time

As the result of further distillations three substances were isolated:

Substance 1, b.p. 60.5-60.8° (17 mm); 10.00 g
Substance 2, b.p. 99.5-101° (15 mm); 21.21 g
Substance 3, b.p. 144.5-145° (15 mm); 8.90 g

Substance 1 was di-sec-butyl formal (Table 2, No. 4); data in the literature: b.p. 157° (730 mm) [21]. Substance 2 was sec-butyl cyclohexyl formal (Table 2, No. 5). Substance 3 was dicyclohexyl formal having d_4^{20} 0.9706; n_D^{20} 1.4709; found MR 61.15, the constants found being close to those already found for this compound (Table 2, No. 1).

Under the conditions of the reaction, therefore, the initial product, sec-butyl cyclohexyl formal, underwent partial symmetrization with formation of di-sec-butyl and dicyclohexyl formals. The overall yield of formals(calculated as unsymmetrical formal) was 63.8%. Taking the total yield of formals as 100%, we obtained:

Di-sec-butyl formal	– 24.9 %
sec-Butyl cyclohexyl formal	– 52.9 %
Dicyclohexyl formal	– 22.2 %

4. 1-(Cyclohexyloxymethyl)pyridinium Chloride ($C_6H_{11}OCH_2NC_5H_5$)Cl and Isopropyl Alcohol $CH_3-CHOH-CH_3$. A mixture of 75.8 g (0.33 mole) of 1-(cyclohexyloxymethyl)pyridinium chloride and 20 g (0.33 mole) of isopropyl alcohol was heated at 100° for 18 hours. The mixture was cooled and then treated as in the preceding experiments. Fractional distillation yielded:

1) Diisopropyl formal: b.p. 55.5-56° (81 mm), 5.84 g (Table 2, No. 2). Data in the literature: b.p. 55.5-56° (81 mm); 5.84 g (Table 2, No. 2), Data in the literature: b.p. 118.5°, d^{20} 0.831 [22]; b.p. 118° [21]; b.p. 120.5-121° (765 mm); d_4^{20} 0.8181; n_D^{20} 1.38413 [23].

2) Cyclohexyl isopropyl formal: b.p. 70-70.5° (6 mm), 16.56 g (Table 2, No. 3).

3) Dicyclohexyl formal: b.p. 152.5-153.0° (20 mm); 9.32 g; d_4^{20} 0.9695; n_D^{20} 1.4705; found MR 61.08

Found %: C 73.60; H 11.39
Calculated %: C 73.73; H 11.42

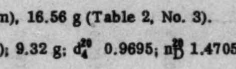
The yield of formals, calculated as unsymmetrical formal, was 55.3%. Taking the total yield of formals as 100%, we obtained 18.4% of diisopropyl formal, 52.2% of cyclohexyl isopropyl formal, and 29.4% of dicyclohexyl formal.

5. 1-(Isopropoxymethyl)pyridinium Chloride ($i-C_3H_7OCH_2NC_5H_5$)Cl and tert-Butyl Alcohol $(CH_3)_3COH$. A mixture of 72.60 g (0.39 mole) of 1-(isopropoxymethyl)pyridinium chloride and 28.67 g (0.39 mole) of tert-butyl alcohol was heated at 100° for 14 hours. The reaction products were treated as in the preceding experiments. The mixture of formals was fractionated through a 25-plate column, and the following formals were obtained:

1) Diisopropyl formal: b.p. 59-59.2° (97 mm); 11.27 g; d_4^{20} 0.8183; n_D^{20} 1.3848; found MR 37.84. The constants found were close to the reported values (Table 2, No. 2).

2) tert-Butyl isopropyl formal: b.p. 71.1-71.5° (96 mm), 10.65 g (Table 2, No. 9).

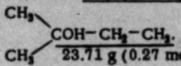
3) Di-tert-butyl formal: b.p. 77-79.5° (96 mm), 5.82 g (Table 2, No. 8). Data in the literature: b.p. 182-185° [24]; b.p. 50-52° (18 mm); d_4^{20} 0.8260; n_D^{20} 1.39904 [25]. The yield of formals, calculated as unsymmetrical formal, was 49.0% Taking the total yield of formals as 100%, we obtained 40.6% of diisopropyl formal, 38.4% of tert-butyl isopropyl formal, and 21.0% of di-tert-butyl formal.

6. 1-(1-Methylheptyloxymethyl)pyridinium Chloride 
$\left(\begin{matrix}CH_3\\C_6H_{13}\end{matrix}\!\!>CH-O-CH_2NC_5H_5\right)Cl$ and tert-Butyl Alcohol $(CH_3)_3COH$. A mixture of 57.70 g (0.22 mole) of 1-(1-methylheptyloxymethyl)pyridinium chloride and 16.59 g (0.22 mole) of tert-butyl alcohol was heated at 120° for 17 hours. Fractional distillation resulted in the isolation of the following substances: di-tert-butyl formal, b.p. 83-84° (99 mm), 2.31 g, the constants found being close to those already found for this compound (Table 2, No. 8); tert-butyl 1-methylheptyl formal, b.p. 128-129° (29 mm), 12.50 g (Table 2, No. 7); and bis(1-methylheptyl) formal, b.p. 183.5-184.5° (27 mm), 11.20 g, d_4^{20} 0.8414; n_D^{20} 1.4323; found MR 84.02, the constants found being close to those found previously (Table 2, No. 6).

The yield of formals, calculated as unsymmetrical formal, was 53.7%. Taking the total yield of formals as

100%, we obtained 8.9% of di-tert-butyl formal, 48.0% of tert-butyl 1-methylheptyl formal, and 43.1% of bis (1-methylheptyl) formal.

7. 1-(Cyclohexyloxymethyl)pyridinium Chloride ($(C_6H_{11}OCH_2NC_5H_5)Cl$) and 2-Methyl-2-butanol



$$\begin{matrix} CH_3 \\ \\ CH_3 \end{matrix}\!\!>\!COH-CH_2-CH_3.$$

A mixture of 61.26 g (0.27 mole) of 1-(cyclohexyloxymethyl)pyridium chloride and 23.71 g (0.27 mole) of 2-methyl-2-butanol was heated at 110-115° for 16 hours. The reaction products were treated as in the preceding experiments. Fractional distillation resulted in the isolation of the following formals:

1) Cyclohexyl 1,1-dimethylpropyl formal, b.p. 119.5-120.5° (23 mm), 5.27 g (Table 2, No. 10).

2) Dicyclohexyl formal, b.p. 155.5-156.5° (27 mm); d_4^{20} 0.9693; n_D^{20} 1.4702; found MR 61.14. The constants are close to those given in Table 2, No. 1. The yield was 8.83 g.

The yield of formals, calculated as unsymmetrical formal, was 26.2%. An appreciable amount of pentene isomers was also obtained.

SUMMARY

1. It was shown that in the reaction of quaternary ammonium salts of the type $(R-O-CH_2-\overset{|}{\underset{|}{N}}-)X$ with secondary and tertiary alcohols formals are formed.

2. When the radical R of the alkoxymethyl group of the quaternary ammonium salt is the same as the radical of the alcohol, symmetrical formals are obtained, but when these radicals are different, three formals, two symmetrical and one unsymmetrical, are formed. The yield of formals was 50-60%.

3. Some of the formals have been prepared and described for the first time, namely: cyclohexyl isopropyl, sec-butyl cyclohexyl, tert-butyl 1-methylheptyl, cyclohexyl 1,1-dimethylpropyl, and tert-butyl isopropyl formals.

LITERATURE CITED

[1] D. N. Kursanov, V. N. Setkina, and V. M Rodionov, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. 1948, No. 2, 228.

[2] V. N. Setkina and D. N. Kursanov, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. 1949, No. 3, 311.

[3] V. N. Setkina and D. N. Kursanov, Bull. Acad. Sci. U.S S.R. Div. Chem. Sci. 1950, No. 4, 386.

[4] V. N. Setkina and D. N. Kursanov, Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci. 1949, No. 2, 190.

[5] D. N. Kursanov and V. N. Setkina, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. 1950, No. 6. 654.

[6] D. N. Kursanov and V. N Setkina, Bull. Acad. Sci. U.S.S R., Div. Chem. Sci. 1949, 3, 274.

[7] F. Litterscheid, Ann. 330, 114 (1904); 316, 157 (1901).

[8] E. Wedekind, Ber., 36, 1384 (1903); German Pat. 135310 of August 31, 1901; C 1902; II, 1164.

[9] V. N Setkina, Synthesis of Substances that confer Hydrophobic Properties on Cellulose, Thesis, Moscow, 1941.

[10] D. N Kursanov and V. N Setkina, J. Appl. Chem. 16, 36 (1943).

[11] S. Sabetau, P. Schving, Bull. Soc. Chim. France [4], 43, 1342 (1928); L. Palfray, S. Sabetau, Bull. Soc. Chim. France [4], 43, 900 (1928).

[12] I. Farren, H. Fife, F. Clark, C. Garland, J. Am. Chem. Soc., 47, 2421 (1925).

[13] F. Litterscheid, Ann. 330, 108 (1904).

[14] L. Stappers, Bull. Acad. roy. Belgique 1904, 1161 1170; C. 1905, I, 921.

[15] H Henze, V. Duff, W. Matthews, I. Melton, E. Forman. J. Am. Chem. Soc., 64, 1222 (1942).

[16] M. Delepine Bull. Soc. chim. France (3) 25, 574 (1901).

[17] V. G. Mkhitaryan, J. Gen. Chem. 8, 1361 (1938); J. Gen. Chem. 9, 1923 (1939).

[18] M. F. Shostakovsky, Vinyl Ethers, Acad. Sci. U.S.S.R. Press, Moscow, 1952, pp. 193-202.

[19] M. Murat, Cathala, J. Pharm. Chim. [7], 6. 289; C. 1912, 11, 1822.

[20] H. Hunter, J. Chem. Soc., 1924, 125. 1389.

[21] A. Skrabal, H. Eger, Z. Phys. Chem. 122, 351 (1926).

[22] M. Arnold, Ann. 240, 199 (1887).

[23] A. Vogel, J. Chem. Soc. 616 (1948).

[24] J. Conant, C. Webb, W. Mendum. J. Am. Chem. Soc., 51, 1246-1955 (1929).

[25]. L. R. Leimu, Suomen Kemistilehti 19B, 66(1946); Chem. Abs. 41, 5442 b (1947).

Received July 29, 1954

Institute of Heteroorganic Compounds
of the U.S.S.R. Academyof Sciences

MACROMOLECULAR COMPOUNDS

COMMUNICATION 77. DEPENDENCE OF THE PROPERTIES OF ALIPHATIC POLYAMIDES HAVING "EVEN" REPEATING UNITS ON THE STRUCTURE OF THE REPEATING UNIT

V. V. Korshak and T. M. Frunze

In a previous communication we pointed out that melting points reported in the literature for some polyamides are incorrect [1]. For example, Coffman and coworkers [2] state that the melting point of 6,8-nylon (polyhexamethylenesuberamide) is 185°, whereas in fact this polyamide melts at 225° [1].

The correct melting points, as determined by us, for some polyamides derived from 1,6-hexanediamine and dicarboxylic acids having even numbers of carbon atoms in their molecules are given in Table 1.

In this table the proportion of amide groupings in the macromolecular chain is given as a percentage of the number of methylene groups. It was found that when the dependence of the melting points of these polyamides on the proportion of amide groupings was represented graphically, the straight line shown in Fig. 1 was obtained.

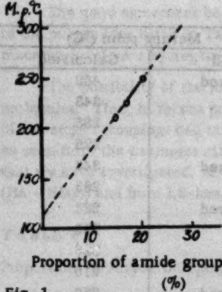


Fig. 1

This straight line is described by the following equation:

$$y = 7x + 110$$

in which y is the melting point (°C) and x is the number of amide groupings expressed as a percentage of the number of methylene groups.

By the use of this equation we have calculated the melting points of some polyamides derived from "even" diamines and "even" dicarboxylic acids, and also of polyamides derived from "even" (the term refers to the number of methylene groups) ω-amino acids and, comparing the results with data reported in the literature [3], we have in some cases obtained good agreement between our calculated values and the values determined experimentally, as can be seen from Table 2.

In other cases the agreement is not so good, and discrepancies of the order of 5, 10, and 15° are obtained.

On the basis of the data in Table 2, we are inclined to attribute the difference between the calculated and experimentally determined values of the melting point to errors in the determination, possibly due to the presence of impurities, such as cresol, which lower the melting point. By the use of the equation given above it is possible to calculated the melting points of polyamides that have not yet been prepared, and also to correct melting points, when this is necessary. Results obtained in this way for polyamides derived from even diamines and even dicarboxylic acids are given in Table 3.

TABLE 1
Melting Points of some Polyhexamethylenealkanediamides [1]

Polyamide	Formula	M.p. (°C)	Amide/methylene ratio (mole-%)
6,6-Nylon	$[-NH(CH_2)_6NH \cdot CO(CH_2)_4CO-]x$	250	20.00
6,7-Nylon	$[-NH(CH_2)_6NH \cdot CO(CH_2)_6CO-]x$	225	16.66
6,10-Nylon	$[-NH(CH_2)_6NH \cdot CO(CH_2)_8CO-]x$	210	14.28

An interesting feature of the law that we have discovered is that the melting points of these polyamides do not depend on the way in which the methylene and amide groups are arranged in the repeating unit of the macromolecule, but depend only on the relative numbers of these groups, as can be seen from the data in Table 4, in which examples are given that illustrate this law.

TABLE 2

Calculated and Experimentally Determined Melting Points of some Polyamides

Melting point (°C)		Polyamide	Formula	Amide/ methylene ratio (mole-%)
Calculated from equation	Found			
250	250	6,6-Nylon	$[-NH(CH_2)_6NH\cdot CO(CH_2)_4CO-]_x$	20.00
250	250	4,8-Nylon	$[-NH(CH_2)_4NH\cdot CO(CH_2)_6CO-]_x$	20.00
226	223	7-Nylon	$[-NH(CH_2)_6CO-]_x$	16.66
226	225	6,8-Nylon	$[-NH(CH_2)_6NH\cdot CO(CH_2)_6CO-]_x$	16.66
210	210	6,10-Nylon	$[-NH(CH_2)_6NH\cdot CO(CH_2)_8CO-]_x$	14.28
197	195	9-Nylon	$[-NH(CH_2)_8CO-]_x$	12.50
197	197	8,10-Nylon	$[-NH(CH_2)_8NH\cdot CO(CH_2)_8CO-]_x$	12.50
180	180	11-Nylon	$[-NH(CH_2)_{10}CO-]_x$	10.00
153	150	17-Nylon	$[-NH(CH_2)_{16}CO-]_x$	6.25

TABLE 3

Calculated Melting Points of some Polyamides

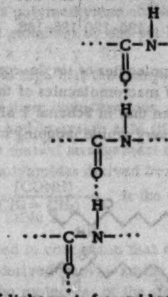
Diamine	Dicarboxylic acid	Melting point (°C)	
		Found	Calculated
1,4-Butanediamine	Oxalic	Not prepared	460
	Succinic	"	343
	Adipic	280	285
	Sebacic	232	226
1,6-Hexanediamine	Oxalic	Not prepared	343
	Succinic	210	285
1,8-Octanediamine	Oxalic	Not prepared	285
	Succinic	"	250
	Adipic	235	226
	Suberic	202	210
1,10-Decanediamine	Oxalic	Not prepared	250
	Succinic	"	225
	Adipic	230	210
	Suberic	Not prepared	197
	Sebacic	194	187

TABLE 4

Melting Points of Polyamides of Different Structure

Amide/ methylene ratio (mole-%)	Polyamide	Formula	M.p.(°C)
12.50	9-Nylon	$[-NH(CH_2)_8CO-]_x$	195
	8,10-Nylon	$[-NH(CH_2)_8NH\cdot CO(CH_2)_8CO-]_x$	197
16.66	7-Nylon	$[-NH(CH_2)_6CO-]_x$	223
	6,8-Nylon	$[-NH(CH_2)_6NH\cdot CO(CH_2)_6CO-]_x$	225
20.00	6,6-Nylon	$[-NH(CH_2)_6NH\cdot CO(CH_2)_4CO-]_x$	250
	4,8-Nylon	$[-NH(CH_2)_4NH\cdot CO(CH_2)_6CO-]_x$	250

The amide groupings, therefore, would appear to take part in the formation of cross links between the chains of different macromolecules, thus impeding the separation of the chains and making it necessary to expend a considerable amount of thermal energy in bringing about the separation of these chains; this behavior is manifested by a rise in melting point that is proportional to the proportion of amide groupings. There can be no doubt that it is not the presence of the amide groupings, as such, that is important, but their ability to interact with one another with the formation of hydrogen bonds according to the scheme



so that a network of linkages is formed between the various macromolecules. These linkages are arranged in a plane, which is inclined at a certain angle to the axis of the macromolecule.

The good agreement between the calculated and experimentally determined proportions of amide groupings in the polyamides listed in Table 5 indicates that in these polyamides all of the amide groupings in any given macromolecule are hydrogen-bonded to amide groupings in neighboring macromelecules.

The possibility of the formation of hydrogen bonds is determined mainly by the stereochemistry of the macromolecules. Thus, in mixed polyamides, even when derived from even diamines and even carboxylic acids, not all of the amide groupings can take part in hydrogen bonding, and this fact is reflected in the melting points, as can be seen from the examples cited in Table 6. This table gives the melting points of mixed-polyamide systems that we have investigated, namely, those prepared from 1,6-hexanediamine adipate + 1,6-hexanediamine suberate (HA + HSub) and from 1,6-hexanediamine adipate + 1,6-hexanediamine sebacate (HA + HSeb).

TABLE 5

Proportions of Amide Groupings, Experimentally Determined and Calculated, in various Polyamides

Polyamide	M.p. (°C)	Amide/ methylene ratio (mole-%)	
		Determined from the melting point	Calculated from the empirical formula
17-Nylon	150	5.71	6.24
11-Nylon	180	10.00	10.00
8,10-Nylon	197	12.43	12.50
9-Nylon	195	12.14	12.50
6,10-Nylon	210	14.28	14.28
6,8-Nylon	225	16.43	16.66
7-Nylon	223	16.14	16.66
4,8-Nylon	250	20.00	20.00
6,6-Nylon	250	20.00	20.00

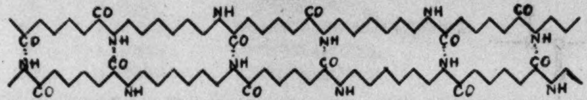
TABLE 6

Melting Points of Mixed Polyamides (°C)

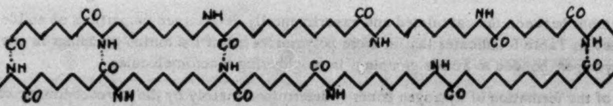
Starting substances	Molar ratio of starting substances						
	1.0+0.0	0.8+0.2	0.6+0.4	0.5+0.5	0.4+0.6	0.2+0.8	0.0+1.0
HA + HSub	250-252	230-237	210-215	-	197-203	210-213	225-227
HA + HSeb	250-252	220-227	190-197	190-195	185-186	190-195	210-212

If, in fact, we represent diagramatically a planar array of macromolecules of single-component polyamides derived from the salt HA (Scheme 1) (or from the salt HSeb) and also of macromolecules of the mixed polyamide derived from the salts HA + HSeb (Scheme 2), then it can be readily seen that in Scheme 1 all the amide groupings can form hydrogen bonds (dotted lines), whereas in Scheme 2 not every amide grouping can form a hydrogen bond.

Scheme 1



Scheme 2



In considering mixed polyamides we must now distinguish between the number of amide groupings and the number of hydrogen bonds, for they are not identical, the former being always greater than the latter.

For such cases we may cast our proposed equation into a more general form:

$$y = 7z + 110\cdot$$

in which $\underline{z} = \underline{kx}$, the coefficient $\underline{k}$ being the fraction of the amide groupings that is hydrogen-bonded.

From the experimentally found melting points we may calculate the number of hydrogen bonds (per 100 methylene groups), compare it with the number of amide groupings, and determine what percentage of these groupings are free. These free amide groupings, which are not bound by hydrogen bonds, evidently play an insignificant part in determining the properties of the given polymer. In Table 7 these quantities are given for the (HA + HSeb) system of mixed polyamides already given in Table 6.

TABLE 7

Proportion of Hydrogen-bonded Amide Groupings in the System (HA + HSeb)

Molar proportions of original substances HA + HSeb	M.p.(°C)	No. of hydrogen bonds per 100 methylenes	No. of amide groupings per 100 methylenes	No. of amide groupings that are not hydrogen-bonded	
				(per 100 amide groupings)	(per 100 methylene groups)
1.0+0.0	250	20.00	20.00	0.0	0.0
0.8+0.2	220	15.71	18.52	15.17	2.81
0.6+0.4	190	11.43	17.24	33.71	5.81
0.4+0.5	190	11.43	16.66	31.40	5.23
0.4+0.6	185	10.71	16.13	33.61	5.42
0.2+0.8	190	11.43	15.15	24.56	3.72
0.0+1.0	210	14.28	14.28	0.0	0.00

The effect of stereochemical factors is particularly clear in polyamides derived from odd amino acids, diamines, and dicarboxylic acids, and this matter will form the subject of the next paper.

In conclusion we will consider some of the inferences that can be made from our proposed equation:

$$y = 7x + 110,$$

When $\underline{x} = 0$, $\underline{y} = 110°$, so that the graph intersects the axis at the point corresponding to the melting points of polyethylene, which has a polymethylene chain free from amide groupings. When $\underline{x} = 1$, $\underline{y} = 117°$, so that increase in the number of amide groupings by one per 100 methylene groups results in a rise in the melting point of the polyamide of 7°. When $x = 100$, $y = 810°$, so that for 2,2-nylon (polyethyleneoxamide) CO. CO. NH $(CH_2)_2$NH– the melting point is so high that the compound decomposes long before this temperature is reached.

On the basis of these considerations, all aliphatic straight-chain polyamides can be regarded as copolymers of ethylene($CH_2 = CH_2$) and isocyanic acid ($H{-}N{=}C{=}O$) and in general their structure can be represented as $(CH_2{=}CH_2)_x(CONH)_y$. The mutual arrangement of these components has no effect on the melting point, as can be seen by a comparison of polyamides derived from ω-amino acids with those derived from dicarboxylic acids and diamines. If the ratio $\frac{[CONH]}{[CH_2 = CH_2]}$ is the same for two or more polyamides, then their melting points will be equal, as can be seen from Table 2.

It must be stated in conclusion that the laws that we found relating the properties (melting point, solubility, etc.) of polyamides derived from ω-amino acids or from diamines and dicarboxylic acids with their structures, always provided that the molecules of the starting substances contain even numbers of methylene groups, present an example of simple and exact relationships that is very rare in the field of macromolecular compounds.

SUMMARY*

1. The dependence of the melting point of an aliphatic polyamide on the relative numbers of amide and methylene groups in the repeating unit is examined.

2. It is shown that as the amide-methylene ratio of an aliphatic polyamide increases, there is a proportional increase in the melting point.

3. An equation is proposed which describes the dependence of the melting point of aliphatic polyamides on the amide-methylene ratio.

4. It is shown that the melting point of an aliphatic polyamide does not depend on the distribution of methylene and amide groups within the repeating unit, but only on the relative numbers of these groups.

5. The results are interpreted on the basis of the view that hydrogen bonding occurs between amide groupings.

6. It is shown that in mixed polaymides not all of the amide groupings are able to form hydrogen bonds.

7. It is suggested that aliphatic polyamides may be regarded as copolymers of ethylene and isocyanic acid.

Received April 7, 1954

N. D. Zelinsky Institute of Organic Chemistry of the
USSR Academy of Sciences

LITERATURE CITED

[1] V. V. Korshak and T. M. Frunze, Bull Acad. Sci. USSR, Div. Chem. Sci. 1955, 163.(T.p.143)**

[2] D. D. Coffman, G. J. Berchet, W. R. Peterson, E. W. Spanagel, J. Polymer Sci. 2, 306 (1947).

[3] V. V. Korshak, Methods of Macromolecular Organic Chemistry, Vol. 1. General Methods for the Synthesis of Macromolecular Compounds, Acad. Sci. USSR Press, Moscow, pp. 449, 450.

---

* Note that this summary refers essentially to polyamides derived from components having an even number of methylene groups —Publisher.

** T.p. = C. B. Translation pagination.

BLANK
PAGE

MACROMOLECULAR COMPOUNDS

COMMUNICATION 73. DEPENDENCE OF THE PROPERTIES OF ALIPHATIC POLYAMIDES HAVING "ODD" REPEATING UNITS ON THE STRUCTURE OF THE REPEATING UNIT

V. V. Korshak and T. M. Frunze

In the preceding communication [1] we examined the dependence of the properties of polyamides having "even" repeating units on the structure of the repeating unit. It was found that there is a linear relationship between the melting point of the polyamide and the number of hydrogen bonds formed by amide groupings (relative to the number of methylene groups):

$$y = 7x + 110,$$

in which y is the melting point (°C) and x is the number of hydrogen bonds formed per 100 methylene groups.

With the aid of this equation we calculated the melting points of a large number of polyamides, and for many of them there was good agreement between observed and calculated values. For other polyamides, however, such agreement was not observed, and this was evidently to be explained, in the case of polyamides having even repeating units, by errors in the data given in the literature, as we succeeded in showing by our own experiments on 6,8-nylon (polyhexamethylenesuberamide)), 6,9-nylon, 6,7-nylon, and other polyamides [2]. By the use of the proposed equation, we calculated melting points for known and unknown even polyamides [1].

However, an attempt to apply this equation to the large group of polyamides having odd repeating units — in which, if derived from a diamine and dicarboxylic acid, at least one of these has an odd number of methylene groups and, if derived from an amino acid, this acid has an odd number of methylene groups — was unsuccessful. In the table we cite melting points from the literature [3] and give our calculated melting points for some polyamides having odd repeating units.

A first glance at Table 1 leads us to suspect that the melting point reported for 4,13 nylon (No. 7) is too high.

The compounds may be divided into four groups according to the extent to which the amide groupings are hydrogen bonded.

The first group comprises polyamides in which about 50% of the amide groupings are hydrogen-bonded (No. 9, 11, 24).

The second group comprises polyamides in which about 75% of the amide groupings are hydrogen-bonded (No. 1, 2,4,8,10,12,13,14,16,18,21,25).

The third group comprises polyamides in which about 85% of the amide groupings are hydrogen-bonded (No. 3,5, 15, 19,22,23).

The forth group comprises polyamides in which more than 90% of the amide groups are hydrogen-bonded (No. 6,7, 17, 20,26).

Within each group there are certain resemblances between the individual compounds.

The first group includes polyamides in which both the original diamine and the original dicarboxylic acid have odd numbers of carbon atoms, which clearly corresponds to a distribution of amide groupings in which only one-half can form hydrogen bonds, as can be seen by reference to the example of 5,7-nylon (No. 9), the hydrogen bonding of which is shown diagrammatically below:

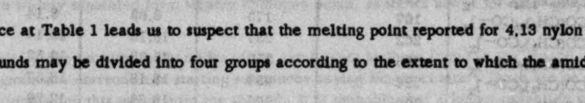
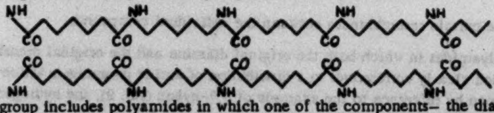


TABLE 1

Observed and Calculated Melting Points of Polyamides having Odd Repeating Units

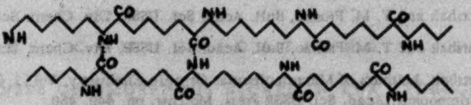
No.	Polyamide	Melting point (°C)		No. of amide groupings per 100 methylene groups	No. of hydrogen bonds per 100 methylene groups	Percentage of amide groupings that are hydrogen-bonded
		Experimentally determined	Calculated from the proportion of amide groupings			
1	$[-NH(CH_2)_5CO-]_x$	215	250	20.00	15.00	75.00
2	$[-NH(CH_2)_7CO-]_x$	178	210	14.28	9.71	68.00
3	$[-NH(CH_2)_9CO-]_x$	175	187	11.11	9.28	83.53
4	$[-NH(CH_2)_4NH{\cdot}CO(CH_2)_5CO-]_x$	233	265	22.22	17.57	79.07
5	$[-NH(CH_2)_4NH{\cdot}CO(CH_2)_7CO-]_x$	223	237	18.18	16.14	88.77
6	$[-NH(CH_2)_4NH{\cdot}CO(CH_2)_9CO-]_x$	209	217	15.38	14.28	92.84
7	$[-NH(CH_2)_4NH{\cdot}CO(CH_2)_{11}CO-]_x$	209	203	13.33	14.28	107.12
8	$[-NH(CH_2)_5NH{\cdot}CO(CH_2)_4CO-]_x$	223	265	22.22	16.14	72.63
9	$[-NH(CH_2)_5NH{\cdot}CO(CH_2)_5CO-]_x$	183	250	20.00	10.43	50.21
10	$[-NH(CH_2)_5NH{\cdot}CO(CH_2)_6CO-]_x$	202	237	18.18	13.14	72.27
11	$[-NH(CH_2)_5NH{\cdot}CO(CH_2)_7CO-]_x$	178	226	16.66	9.71	58.28
12	$[-NH(CH_2)_5NH{\cdot}CO(CH_2)_8CO-]_x$	195	217	15.38	12.14	78.93
13	$[-NH(CH_2)_5NH{\cdot}CO(CH_2)_9CO-]_x$	175	203	13.33	9.00	67.52
14	$[-NH(CH_2)_5NH{\cdot}CO(CH_2)_{11}CO-]_x$	176	197	12.50	9.43	75.32
15	$[-NH(CH_2)_5NH{\cdot}CO(CH_2)_{12}CO-]_x$	178	192	11.76	9.71	82.57
16	$[-NH(CH_2)_5NH{\cdot}CO(CH_2)_{14}CO-]_x$	167	183	10.52	8.14	77.37
17	$[-NH(CH_2)_5NH{\cdot}CO(CH_2)_{18}CO-]_x$	167	170	8.69	8.14	93.67
18	$[-NH(CH_2)_6NH{\cdot}CO(CH_2)_5CO-]_x$	202	237	18.18	13.14	72.27
19	$[-NH(CH_2)_6NH{\cdot}CO(CH_2)_7CO-]_x$	205	217	15.38	13.57	88.23
20	$[-NH(CH_2)_7NH{\cdot}CO(CH_2)_4CO-]_x$	226	237	18.18	16.57	91.14
21	$[-NH(CH_2)_7NH{\cdot}CO(CH_2)_5CO-]_x$	196	226	16.66	12.28	73.71
22	$[-NH(CH_2)_7NH{\cdot}CO(CH_2)_8CO-]_x$	187	203	13.33	11.00	82.52
23	$[-NH(CH_2)_9NH{\cdot}CO(CH_2)_4CO-]_x$	204	217	15.38	13.42	87.25
24	$[-NH(CH_2)_9NH{\cdot}CO(CH_2)_7CO-]_x$	163	197	12.50	7.57	49.22
25	$[-NH(CH_2)_9NH{\cdot}CO(CH_2)_{10}CO-]_x$	175	192	11.76	9.28	78.91
26	$[-NH(CH_2)_{10}NH{\cdot}CO(CH_2)_{11}CO-]_x$	172	176	9.52	8.86	93.06

A peculiarity of these macromolecules is that they are not symmetrical with respect to the axis of the molecule, since the CO and NH groups are each disposed on one side only of the molecule, so that if they have the other possible mutual arrangement in the plane no hydrogen bonds can form:



The second group includes polyamides in which one of the components– the diamine or dicarboxylic acid — has an odd number of carbon atoms, and the other component has an even number of carbon atoms. As exceptions there are some compounds in which both components are odd, their presence here being associated, possibly, with errors in the determination of the melting points or with a general tendency for the melting point to rise with increase in the length of the repeating unit. This group contains also some polyamides derived from ω-amino acids containing odd number of methylene groups in their molecules.

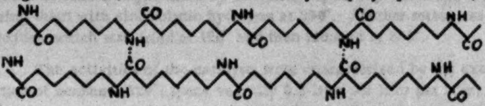
The scheme of hydrogen bonding in one of the members of this group is shown below:



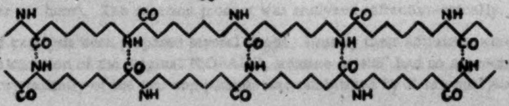
The hydrogen bonds in 5,6-nylon, which is shown in the diagram, alternate in pairs, but the intermediate pairs of amide groupings also form hydrogen bonds, though they are weaker owing to the greater distance of the groups with which they are linked. It would appear that two weak hydrogen bonds of this sort have the same effect as one normal hydrogen bond, so that the overall result is the same as if 75% of the amide groups formed hydrogen bonds. The possibility that this might occur was pointed out by Champetier and Aelion [4].

Polyamides derived from amino acids having an odd number of methylene groups have molecules of the vector type, i.e. the arrangement of groups differs according to the direction in which the molecule is examined - from right to left, or from left to right. The number of hydrogen bonds formed will therefore differ according as all the macromolecules are turned in the same direction or are turned alternately in different directions. In the first case only one-half of the amide groupings can form hydrogen bonds (I), whereas in the second case all can form hydrogen bonds (II), as shown below for 6-nylon (polycaprolactam):

I



II



It would appear that the first variant represents the normal arrangement of molecules (I), and the amide groupings that are more widely separated form weaker hydrogen bonds, as shown above for other polyamides of the second group.

The third group includes polyamides of the same types as those found in the second group, but the polymers of the third group are derived from starting substances having longer chains. There are no other peculiarities of structure distinguishing this group from the second. It is probable that a longer repeating unit permits the formation of a larger number of hydrogen bonds on account of the greater mobility of the macromolecule chain and the possibility of the folding of individual chains.

The fourth group includes substances derived from compounds having still longer chains, so that still more amide groupings can form hydrogen bonds. This group includes 5,20- and 10,13-nylons.

Increase in the lengths of the molecules of the original reactants, therefore, facilitates the formation of hydrogen bonds between amide groupings, and it may be expected that, when the repeating unit is sufficiently long, even polyamides derived from odd diamines and dicarboxylic acids will be able to form hydrogen bonds with the participation of all the amide groupings present, so that complete agreement will be found between the observed and calculated melting points.

SUMMARY

1. The relationship between the properties of polyamides having odd repeating units and the structure of their repeating units is examined.

2. It is shown that in polyamides having odd repeating units not all of the amide groupings are able to form hydrogen bonds.

3. It is shown that lengthening of the molecules of the original monomeric reactants creates more favorable conditions for the hydrogen bonding of the amide groupings of polyamides.

Received April 7, 1954

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

LITERATURE CITED

[1] V. V. Korshak and T. M. Frunze, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 756. (T.p.673)*

[2] V. V. Korshak and T. M. Frunze, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 163. (T.p.143)*

[3] V. V. Korshak, Methods of Macromolecular Organic Chemistry, Vol., 1, General Methods for the Synthesis of Macromolecular Compounds, Acad. Sci. USSR Press, Moscow, pp. 449, 450.

[4] G. Champetier, R. Aelion, Bull. Soc. Chim. France, 1948, 683.

---

* T. p. = C. B. Translation pagination.

BRIEF COMMUNICATIONS

CATALYTIC INERTNESS OF AMORPHOUS NICKEL IN THE HYDROGENATION OF BENZENE AND THE DEHYDROGENATION OF CYLCOHEXANE

A. M. Rubinshtein, L. Kh. Freidlin, and N. V. Borunova

While studying the effect of the conditions of calcining a mixture of nickel and aluminum hydroxides on the activity of the Ni-Al_2O_3 catalyst derived from the product, we came across an interesting example of the formation of inactive nickel catalysts of amorphous structure.

A catalyst containing 30% of nickel and 70% of alumina was prepared via the aluminate from molar solutions of nickel and aluminum nitrates and 30% caustic soda solution. The washed precipitate was dried at 110-120° and then formed into a 3 x 3 mm cylinder. One series of catalysts was prepared from the above-described mixture of hydroxides by calcining separate portions for 6-12 hours at 300°, 350°, and 425° and then reducing them with electrolytic hydrogen at 350°. Another series was prepared directly from the mixture of hydroxides, which was dried at 120° and then reduced at 350°.

The activities of the catalysts were characterized by the extent to which they promoted the hydrogenation of benzene (120°; space velocity 0.3 liter per liter per hour) and the dehydrogenation of cyclohexane (300°; space velocity 0.3 liter per liter per hour). The reaction product was analyzed refractometrically.

The above-described series of catalysts were prepared several times. Usually their activities were satisfactorily reproducible and prior calcination of the original NiO-Al_2O_3 mixture at 425° had no appreciable effect. In these catalyst samples the crystallinity of the two components was established by X-ray analysis.

The catalysts numbered 1 to 4 in the table, which were prepared by the same method, behaved quite differently. The table shows that catalysts prepared from a mixture of nickel and aluminum oxides calcined for 10-12 hours at 425° (No. 1, 2, and 3) or even 350° (No. 4) and then reduced with hydrogen at ordinary pressure (No. 1) or at a pressure of 500 atm (No. 2, 3, and 4) were completely inactive in the hydrogenation of benzene and the dehydrogenation of cyclohexane. The uncalcined catalysts, after reduction with hydrogen at ordinary pressure (No. 6) or at 500 atm (No. 7 and 8), were fairly active. It was clear that the difference in activity could be caused only by the difference in the pretreatment of the mixture of oxides (low-temperature drying, on the one hand, and calcination, on the other). Catalyst No. 5, which received a preliminary calcination at 300° and was reduced with hydrogen under pressure, was also active. All these catalysts gave X-ray diffraction patterns in which there was a fairly intense even background and (with the exception of catalysts No. 1 and 4) some lines of low or very low intensity corresponding to the interplanar spacings (d) shown in the table. When these results are compared with data given in tables for Ni [1] and γ-Al_2O_3 [2], it is readily seen that the X-ray photographs obtained from the catalysts did not give the complete diffraction pictures of Ni and Al_2O_3; moreover, the lines were much weaker than those given by the pure substances owing to their mutual dilution in the mixture and their imperfect crystallinity. None of the lines was in the form of a doublet. Also, the lines corresponding to d = 1.98-2.04 A, 1.75-1.77 A, and 1.24 A could have been formed both by reflection from Ni crystals and by reflection from γ-Al_2O_3 crystals. Some of the departures from the values of d given in tables could have resulted from defects in the crystals themselves and from high experimental errors arising from the diffuseness and low intensity of the lines obtained. When the structural data are considered together with the data on the activities of catalysts No. 1 and 4 (amorphous) and No. 2 and 3, it is found that in the last two catalysts also, the nickel was either amorphous or in the form of crystals having linear dimensions below the limit of resolution of the X-ray structure method; γ-Al_2O_3, on the other hand, was present in a crystalline form. In catalysts No. 5-8 each component was present partly in the amorphous and partly in the crystalline form. Before being reduced, the calcined mixture of oxides gave an amorphous photograph, which is in accord with the results of other workers [3]. It was thus shown that the catalytically inert samples were amorphous to X-rays. The amorphous nickel could have arisen during calcination by reaction between NiO and Al_2O_3 with formation of the spinel $NiAl_2O_4$ the structure of which would be broken down in the subsequent treatment with hydrogen with the separation of nickel and alumina. Under these conditions of formation, nickel atoms are not able to associate together to form crystals of appreciable size.

TABLE

Catalyst No.	Calcination conditions		Conditions of reduction at 350°		Hydrogenation of benzene at 120° (%)	Dehydration of cyclohexane at 300° (%)	Lines on X-ray diffraction photographs of catalysts (d in A)
	Temperature (°C)	Duration (hours)	Duration (hours)	Hydrogen pressure (atm)			
1	425	10	26	1	-	0.0	No lines present
2*	425	10	1	500	0.0	-	1.98; 1.77
3	425	10	10	500	0.2	-	2.44; 2.03; 1.75; 1.59
4	350	12	5	500	0.0	-	No lines present
5	300	6	5	500	38.4	-	1.98; 1.76
6	120	6	26	1	-	62.0	2.01
7	120	6	2	500	30.2	-	1.99; 1.50
8	120	6	5	500	96.8	61.0	2.04; 1.76; 1.60; 1.49; 1.30; 1.24

A temperature of 350-425° apparently represents a lower limit for chemical interaction between NiO and Al_2O_3, for calcination at 300° has almost no effect on the activity of the catalyst. It may be considered that the temperature at which reaction between NiO and γ-Al_2O_3 begins is not below this level. Such a low temperature (see [3]) for the formation of a spinel is probably to be explained by the large surface of contact of the components resulting from the homogenization of the mixture of hydroxides under the influence of some factors operating during the precipitation process which we have not taken into account.

According to the multiplet theory of catalysis [4], owing to the absence of structural correspondence between the catalyst and the reacting molecule, randomly distributed nickel atoms are unable to accelerate the hydrogenation of benzene or the dehydrogenation of cyclohexane. It might be expected, however, that the hydrogenation of a C=C bond would occur on such a catalyst, i.e. that a reaction of the doublet type would occur. It was, in fact, found that, in presence of catalyst No. 4 calcined at 350° for 12 hours, 3-octene treated at 130° at a space velocity of 0.2-0.3 was hydrogenated to the extent of 67-69%. For the hydrogenation of a double bond, therefore, the catalysts containing amorphous nickel were found to be active. This may be explained by the occurrence on the surface of pairs of nickel atoms separated by a distance of about 2.49 A, which is the distance necessary for the doublet adsorption of an olefin [5].

Our observations on this case of the formation of nickel-alumina catalysts containing amorphous nickel show that in the preparation of catalysts of this type it is necessary to avoid the formation of homogeneous systems during the precipitation of the hydroxides.

Received February 18, 1955

N. D. Zelinsky Institute of Organic
Chemistry of the USSR Academy of
Sciences

LITERATURE CITED

[1] A. I. Kitaigorodsky. X-Ray Structure Analysis of Finely Crystalline and Amorphous Substances, State Tech. Press, 1952; Hannawalt, Ind. Eng. Chem. 10, 495 (1938).

[2] G. S. Zhdanov, V. P. Kotov, and G. D. Lyubarsky, in the Collection "Problems of Kinetics and Catalysis", 5, Acad. Sci. USSR Press, 1948, p. 25.

[3] W. O. Milligan, L. Merten, J. Phys. Chem. 50, 465 (1946).

[4] A. A. Balandin, Prog. Chem. 4, 1104 (1935); 10, 263 (1941); J. Russ. Phys. Chem. Soc. 61, 909 (1929).

[5] G. Twigg, E. Rideal, Trans. Faraday. Soc. 36, 533 (1940).

---

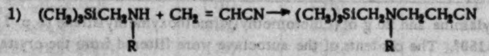
* The sample was reduced at 400°.

CYANOETHYLATION OF ORGANOSILICON AMINES

V. F. Mironov, A. D. Petrov, and N. A. Pogonkina

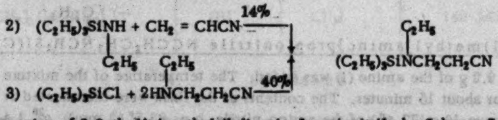
We have recently [1] carried out the cyanoethylation of some organosilicon alcohols in which silicon was attached to the α- or γ-carbon.

In the present investigation we have shown that, like amines that do not contain silicon [2], organosilicon amines in which silicon is attached to the α-carbon are also readily cyanoethylated:



$$1)\quad (CH_3)_3SiCH_2\underset{\displaystyle R}{N}H + CH_2 = CHCN \rightarrow (CH_3)_3SiCH_2\underset{\displaystyle R}{N}CH_2CH_2CN$$

When R was ethyl, reaction occurred readily in absence of catalysts with evolution of heat. When R was phenyl, cyanoethylation occured only in presence of acetic acid as catalyst. On the other hand, silylamines, in which silicon is attached directly to nitrogen, behaved like the silanols and reacted with difficulty after long heating with acrylonitrile (Scheme 2):



$$2)\quad (C_2H_5)_3Si\underset{\displaystyle C_2H_5}{N}H + CH_2 = CHCN \xrightarrow{14\%} (C_2H_5)_3Si\overset{\displaystyle C_2H_5}{N}CH_2CH_2CN$$

$$3)\quad (C_2H_5)_3SiCl + 2H\overset{\displaystyle C_2H_5}{N}CH_2CH_2CN \xrightarrow{40\%} (C_2H_5)_3Si\overset{\displaystyle C_2H_5}{N}CH_2CH_2CN$$

The formation of 3-[ethyl(trimethylsilyl)amino]propionitrile by Scheme 2 was proved by a confirmatory synthesis by Scheme 3.

There is only one reference in the literature to the synthesis of the salt of a silicon-containing quaternary ammonium base, namely, the product of the action of CH_3I on $(CH_3)_3SiCH_2N(CH_3)_2$ [3]. We have synthesized five new quaternary ammonium iodides (white crystalline powders, readily soluble in water). An attempt to prepare the same salts by the action of trialkyl(1-iodoalkyl)silanes on tertiary amines did not succeed, even under severe conditions. For example, treatment of $(C_2H_5)_3N$ with $ICH_2Si(CH_3)_3$ at 200° for ten hours gave an insignificant amount of a substance of m.p. 256° which did not contain silicon. Moreover, tertiary silylamines do not form silicon-containing quaternary ammonium salts with alkyl iodides. For example, when a mixture of $(C_2H_5)_3SiN(C_2H_5)_2$ and CH_3I was allowed to stand for ten days, only a very small amount of brown precipitate formed, and this did not contain silicon.

EXPERIMENTAL

N-[(Trimethylsilyl)methyl]ethylamine $C_2H_5HNCH_2Si(CH_3)_3$ (I)

N,N'-Bis[(trimethylsilyl)methyl]ethylamine $C_2H_5N[CH_2Si(CH_3)_3]_2$ (II)

A mixture of 160 g of ethylamine and 150 g of (chloromethyl)trimethylsilane [4] was heated in an autoclave at about 150° for ten hours (with a break overnight). The contents of the autoclave were then treated with caustic soda of approximately 10% strength, and the organic layer was separated and dried with sodium sulfate. Distillation through a column having an efficiency of 15-20 theoretical plates gave 83.5 g (51%) of the amine (I), b.p. 121.2° (759 mm); n_D^{20} 1.4155; d_4^{20} 0.7594; found MR 43.33; calculated MR 43.18.

Found %: H 13.16; 13.07; C 54.79; 54.91; Si 21.31; 21.52

$C_6H_{17}NSi$. Calculated %: H 13.05; C 54.89; Si 21.37;

The distillation gave also 17.7 g (15.4%) of the amine (II), b.p. 194.5° (760 mm); n_D^{20} 1.4349; d_4^{20} 0.7914; found MR 71.68; calculated MR 71.50.

Found %: H 12.45; 12.40; C 55.31; 55.15; Si 25.65; 25.88

$C_{10}H_{27}NSi_2$. Calculated %: H 12.51; C 55.23; Si 25.80

The organosilicon amines (III) and (IV) were prepared under similar conditions.

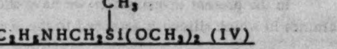
N-[(Trimethylsilyl)methyl]diethylamine $(C_2H_5)_2NCH_2Si(CH_3)_3$ (III)

A. A mixture of 91 g of diethylamine and 61.3 g of (chloromethyl)trimethylsilane was heated in an autoclave at 150° for eight hours. The product isolated was 57.6 g (72.5%) of the amine (III), b.p. 148.2° (740 mm); n_D^{20} 1.4232; d_4^{20} 0.7692; found MR 52.76; calculated MR 52.61.

Found %: H 13.31; 13.44; C 60.55; 60.61; Si 17.59; 17.27

$C_8H_{21}NSi$. Calculated %: H 13.28; C 60.30; Si 17.61

B. A mixture of 46 g of diethylamine and 30 g of (chloromethyl)trimethylsilane was boiled for 31 hours (with breaks overnight). The precipitate was filtered off, and 7.5 g (19%) of the amine (III) was obtained. Boiling of the filtrate for a further 53 hours gave a further 5.3 g of amine, the total yield being 32.4%.



N-[(Dimethoxymethylsilyl)methyl]ethylamine $C_2H_5NHCH_2\overset{CH_3}{\overset{|}{Si}}(OCH_3)_2$ (IV)

A mixture of 23.2 g of ethylamine and 20 g of (chloromethyl)dimethoxymethylsilane (b.p. 139.5°) was heated in an autoclave for four hours at 150°. The contents of the autoclave were filtered from the crystalline precipitate, which was washed with dry ether. Distillation gave 5.4 g (25.6%) of the amine (IV), b.p. 156.5° (750 mm); n_D^{20} 1.4118; d_4^{20} 0.9120; found MR 44.52; calculated MR 44.54.

Found %: H 10.31; 10.41; C 44.16; 44.37; Si 17.11; 16.86

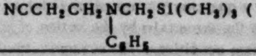
$C_6H_{17}NO_2Si$. Calculated %: H 10.50; C 44.14; Si 17.19

3-{Ethyl[(trimethylsilyl)methyl]amino}propionitrile $NCCH_2CH_2\overset{C_2H_5}{\overset{|}{N}}CH_2Si(CH_3)_3$ (V)

To 3.7 g of acrylonitrile 9.2 g of the amine (I) was added. The temperature of the mixture rose to about 40° and was kept at this level for about 15 minutes. The contents of the flask were then heated at about 60° for 12 hours. Vacuum distillation gave 10 g (77.4%) of the amino nitrile, b.p. 83.5° (3 mm); n_D^{20} 1.4466; d_4^{20} 0.8612; found MR 57.14; calculated MR 57.07.

Found %: H 11.04; 10.95; C 58.66; 58.66; Si 15.42; 15.45

$C_9H_{20}N_2Si$. Calculated %: H 10.93; C 58.64 Si 15.22

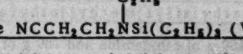


3-{N-[(Trimethylsilyl)methyl]anilino}propionitrile $NCCH_2CH_2\underset{C_6H_5}{\underset{|}{N}}CH_2Si(CH_3)_3$ (VI)

A mixture of 3.2 g of glacial acetic acid, 10 g of acrylonitrile, and 20.6 g of N-[(trimethylsilyl)methyl] aniline [3] was heated at about 130° for 24 hours. Vacuum fractionation gave 18.3 g (68.6%) of the amino nitrile (VI), b.p. 199-201° (6 mm); n_D^{20} 1.5388; d_4^{20} 1.9886; found MR 73.60; calculated MR 72.01.

Found %: H 8.67; 8.60; C 67.41; 67.40; Si 12.30; 11.82

$C_{13}H_{20}N_2Si$. Calculated %: H 8.67; C 67.19; Si 12.07



3-[Ethyl(trimethylsilyl)amino]propionitrile $NCCH_2CH_2\overset{C_2H_5}{\overset{|}{N}}Si(C_2H_5)_3$ (VII)

A. A mixture of 10 g of acrylonitrile and 19.3 g of N,1,1,1-tetraethylsilylamine [5] was heated at 77-80° for 61 hours. Distillation gave 10.7 g of unchanged silylamine and 4 g (13.6%) of the amino nitrile (VII), b.p. 262-265° (740 mm); n_D^{20} 1.4575; d_4^{20} 0.8914; found MR 64.82; calculated MR 65.18.

B. Chlorotriethylsilane (65 g) was added to a stirred solution of 92.7 g of 3-ethylaminopropionitrile in 250 ml of absolute ether. On the next day the precipitate was filtered off and the filtrate was vacuum-distilled twice. The product isolated was 36.5 g (40%) of the amino nitrile (VII) b.p. 265-266° (745 mm); n_D^{20} 1.4590; d_4^{20} 0.8923; found MR 65.11; calculated MR 65.18.

Found %: H 11.51; 11.37; C 61.78; 61.70; Si 12.61; 12.48

$C_{11}H_{24}N_2Si$. Calculated %: H 11.39; C 62.20; Si 13.21

Diethylmethyl[(trimethylsilyl)methyl]ammonium iodide $I[(CH_3)_3SiCH_2\overset{+}{N}(C_2H_5)_2CH_3]$ (VIII)

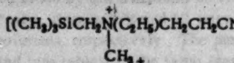
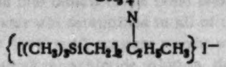
Methyl iodide (6 g) was added to a solution of 3.2 g of the amine (III) in 70 ml of absolute ether. After six days the precipitate formed was filtered off, washed with ether, and dried in a vacuum. The product was 6 g of the substance (VIII), m.p. 118°. After three days a further 0.2 g of the substance (VIII) came down from the filtrate, i.e. the yield attained 100%.

Found %: C 36.09; 36.10; H 8.25; 8.25; Si 9.11; 9.47; I 41.92; 42.06

$C_9H_{24}SiNI$. Calculated %: C 35.88; H 8.03; Si 9.31 I 42.13

In a similar way the iodides of other silicon-containing quaternary ammonium bases were obtained (see table). The analyses of these compounds for C, H, Si, and I were quite satisfactory.

TABLE

Quaternary ammonium salt	Starting substances		M.p. (°C)	No. of days	Yield (%)
	Amine	RI			
$[(CH_3)_3SiCH_2\overset{+}{N}(C_2H_5)_2CH_3]I^-$	(III)	CH_3I	118	6 10	99.5 100
$[(CH_3)_3SiCH_2\overset{+}{N}(C_2H_5)_3]I^-$	(III)	C_2H_5I	170	9	100
$[(CH_3)_3SiCH_2N(C_2H_5)_2C_3H_5]I^-$	(III)	C_3H_5I	144-146	10	80
 $[(CH_3)_3SiCH_2\overset{+}{\underset{\underset{CH_3}{\vert}}{N}}(C_2H_5)CH_2CH_2CN]I^-$	(V)	CH_3I	190	12 53 82	47 72.5 85
 $\{[(CH_3)_3SiCH_2]_2\overset{\overset{+}{N}}{\vert}C_2H_5CH_3\}I^-$	(II)	CH_3I	140-142	4 15 45	15 93.5 96.5

SUMMARY

1. It is shown that it is possible to effect the cyanoethylation of organosilicon secondary amines, both those in which silicon is attached to the α-carbon and those in which silicon is attached directly to nitrogen.

2. It is shown that there is a great difference in behavior between these two classes of organosilicon amines in their reactions with alkyl iodides and with acrylonitrile.

Received March 16, 1955

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

LITERATURE CITED

[1] A. D. Petrov, V. F. Mironov, and N. A. Pogonkina, Proc. Acad. Sci. USSR 100, No. 1, 81 (1955).

[2] Reactions and Methods of Investigating Organic Compounds, Moscow and Leningrad, 2, 1952, p. 75.

[3] J. E. Noll, J. L. Speier, B. F. Daubert, J. Am. Chem. Soc., 73, 3867 (1951).

[4] V. F. Mironov and N. A. Pogonkina, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 1, 182. (T.p.161) *

[5] E. Larsonn, O. Mjörne, Trans. Chalm. Univ. 87, 29 (1949).

---

* T. p. = C. B. Translation pagination.

BLANK
PAGE

EFFECT OF THE STRUCTURAL FACTOR ON THE CATALYTIC DECOMPOSITION OF ALCOHOLS VARYING IN MOLECULAR WEIGHT

A. M. Rubinshtein and N. A. Pribytkova

In a previous investigation [1], in which a simple dehydrating catalyst, alumina, was used, it was observed that the decomposition of alcohols having molecules of different sizes proceeded at different rates over the same sample of catalyst, and this behavior was considered to be associated with the structural characteristics of the catalyst (dimensions of the elementary crystals and the diameters of the pores). We have investigated this phenomenon in greater detail for magnesia catalysts.

The magnesia catalysts designated as I, II, III, and IV were prepared from precipitated magnesium hydroxide obtained by the treatment of 10% magnesium nitrate solution with 10% ammonia at 0°, 20°, 60°, and 100°, respectively. Catalysts V and VI were prepared from the precipitates obtained at 20° from 1% and 50% magnesium nitrate solutions, respectively. The precipitates of hydroxide were washed until reaction for nitrate was negative, converted into tablets in the same press, dried at 110-120°, and calcined in air for six hours at 425-450°. The residual water was determined in all of the catalysts by the calcination of test samples (which were also tested for activity) at 1000° until constant weight was attained. The specific surface was determined by the adsorption of iodine from carbon tetrachloride solution, the procedure described by Zettlemoyer and Walker [2] being used. The linear dimensions of the crystals were established by X-ray analysis from the half-widths of the reflections from the (002), (022), and (222) planes.

The catalytic activity of the samples was determined a) from the rate of decomposition of absolute ethyl alcohol at 435°, 450°, and 465°, the space velocity being 2.7 liters per liter per hours, and b) - for Catalysts I, V, and VI —from the rates of decomposition of absolute ethyl, n-butyl, isopentyl, and n-octyl alcohols at 450°, the space velocity being maintained constant in one series of experiments (at 2.7) and being varied so that the velocities were equimolecular in another series. The experiments were carried out in a continuous-flow system, and the weight of catalyst taken was constant. The catalyst was contained in a Vaskevich reactor [3] mounted in an electric block furnace, and the rate at which the alcohol was passed into the reactor was maintained constant by means of an automatic dispenser [4].

The liquid reaction products collected in a receiver to which a reflux condenser was attached, and the gaseous products were collected over saturated brine and analyzed for hydrogen and olefin contents (dehydrogenation and dehydration). The activity was expressed as milliliters of gaseous product (hydrogen + olefin) separating under the conditions of the experiment in unit time per gram of catalyst. The selectivity coefficient was expressed as a fraction, representing the contribution made by dehydrogenation to the overall result of the two reactions.

X-Ray structure analysis showed that the samples under investigation consisted of magnesium oxide having a constant lattice, the variations from preparation to preparation being within the limits of experimental error. The mean linear dimensions of the crystals did not vary greatly among the samples (Table 1). Calcination at 1000° generally resulted in an increase by a factor of 1.3-1.5 in the mean linear dimension of the crystals. Over the temperature range investigated, and also from sample to sample, the selectivity varied very little. The fact that catalysts calcined at 1000° had greater selectivity coefficients indicates that the removal of water from the catalysts alters the ratio of the rates of dehydrogenation and dehydration in favor of dehydrogenation. The 50% reduction in the overall activity after calcination at 1000° is evidently the result of sintering and reduction in surface, which amounted to as much as 75-80% when constant weight was attained.

Experiments with alcohols containing different numbers of carbon atoms in their molecules showed (Table 2) that not only the activity, but also the selectivity, is dependent on the size of the alcohol molecule. Both at space velocities of 2.7 (Table 2, A) and at equimolecular rates (Table 2, B), there is an appreciable variation in overall specific activity, which for equimolecular rates is particularly marked as we pass from ethyl alcohol to butyl alcohol; this may result from the differences in effective specific surface [1] between one alcohol and another; some of the pores, which are accessible to the small ethyl alcohol molecule, are excluded from the process when the larger molecules of butyl and higher alcohols are reacting. The change in the selectivity of the catalysts with increase in the size of the alcohol molecule cannot, however, be explained by a change in the

TABLE 1

Catalyst No.	Residual Water (%)	Specific surface (sq.m/g)	Linear dimension of MgO crystals (A)	Activity*	Selectivity coefficient
I	2.15	104(27)	66(103)	42.9 79.0 (32.7) 91.0	0.77 0.74 (0.86) 0.74
II	3.25	132(29)	51(83)	52.3 82.6 (24.9) 107.6	0.77 0.72 (0.83) 0.70
III	3.50	131	57	42.8 64.3 99.7	0.75 0.72 0.72
IV	2.95	132(33)	59(83)	34.8 61.7 (27.0) 87.3	0.78 0.77 (0.84) 0.74
V	2.64	111(32)	59(70)	30.3 61.3 (37.6 84.4	0.76 0.72 (0.86) 0.70
VI	2.04	63(36)	82(80)	23.2 44.8 (31.7) 80.6	0.76 0.73 (0.83) 0.75

---

* At 435°, 450°, and 465°, the results obtained at 450° being underlined. The results given in parentheses are for samples calcined at 1000°.

TABLE 2

Catalyst No.	Ethyl alcohol		Butyl alcohol		Isopentyl alcohol		Octyl alcohol	
	Activity	Selectivity coefficient	Activity	Selectivity coefficient	Activity	Selectivity coefficient	Activity	Selectivity coefficient
A. Space velocity 2.7 liters per liter per hour; 450°								
I	79.0	0.74	57.2	0.87	40.3	0.94	40.3	0.89
V	60.6	0.71	52.0	0.92	40.2	0.93	43.5	0.87
VI	42.8	0.73	37.2	0.9	17.9	0.94	28.4	0.86
B. Equimolecular rates (space velocities of 2.7, 4.6, 5.4, and 8.1 liters per liter per hour, respectively); 450°								
I	79.0	0.74	27.3	0.96	26.9	0.95	27.0	0.93
V	60.6	0.71	41.7	0.95	30.3	0.95	29.6	0.92
VI	42.8	0.73	15.9	0.94	–	–	15.6	0.94

effective specific surface. Here the operating factor is a structural one: a screening of part of the active centers as the dimensions of the molecules being adsorbed are increased. According to the multiplet theory [5] it is one of the ways in which a "framed" radical affects a process. Since the adsorbed group CH_2OH of the alcohol molecule is at a large angle to the catalyst surface in dehydrogenation, whereas the adsorbed group CH_2-CH_2OH is at a small angle in dehydration, the screening effect should show itself as a very much greater reduction in activity in dehydration reactions with increase in the size of the alcohol molecule, as compared with the reduction in activity in dehydrogenation reactions. It is in fact found that, as we pass from ethyl alcohol to butyl alcohol, dehydration activity is reduced 7-20 fold (Table 2, B), but hydrogenation activity only twofold. This results in an increase in the selectivity coefficient. If we take the doublet adsorption scheme [5] as the basis for our considerations and take the C−C distance in alcohols to be 1.54 A with tetrahedral valency angles [6], it can be readily shown that the ethyl alcohol molecule should fit on a magnesium oxide surface (d = 2.40 A) in the position required by the dehydration scheme with preservation of valency angles without screening of the surface and without overlapping (data for the calculations are given in [7]). For butyl alcohol however, and still more for higher alcohols, some screening of the surface is inevitable, and the occurrence of such screening provides the explanation of the observed increase in the selectivity coefficient.

Received April 1, 1955

N. D. Zelinsky Institute of Organic Chemistry of
the USSR Academy of Sciences

LITERATURE CITED

[1] A. M. Rubinshtein, V. E. Vasserberg, and N. A. Pribytkova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, 323. (T.p. 325)*

[2] A. C. Zettlemoyer, W. C. Walker, Ind. Eng. Chem. 39, 69 (1947).

[3] D. N. Vaskevich, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1946, 325.

[4] A. M. Levit and L. Kh. Freidlin, Works Lab. 16, 244 (1950).

[5] A. A. Balandin, Jubilee Collection in honor of the Thirtieth Anniversary of the Great October Socialist Revolution, Part 1, Acad. Sci. USSR Press, 1947, p. 637.

[6] A. A. Balandin and Ya. T. Eidus, Proc. Acad. Sci. USSR 49, 680 (1945).

[7] S. Twigg, E. Rideal, Trans. Faraday Soc. 36, 533 (1940).

---

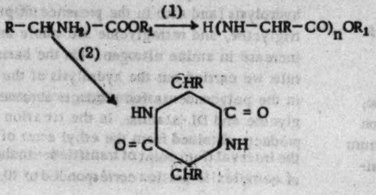
* T.p. = C. B. Translation pagination.

BLANK
PAGE

QUANTITATIVE DETERMINATION OF 2,5-PIPERAZINEDIONES IN THE PRODUCTS OF THE POLYCONDENSATION OF ESTERS OF α-AMINO ACIDS

K. T. Poroshin, T. D. Kozarenko, and Yu. I. Khurgin

It is known that the polycondensation of esters of α-amino acids goes in two directions: 1) the formation of linear polypeptides, and 2) the formation of cyclic dipeptides, i.e. 2,5-piperazinediones (diketopiperazines):



$$R-CH(NH_2)-COOR_1 \xrightarrow{(1)} H(NH-CHR-CO)_nOR_1$$

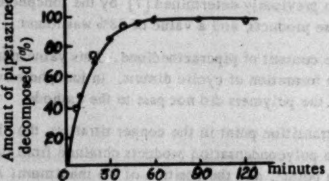


Fig. 1. Curve for the hydrolysis of 2,5-piperazinedione in 0.1 N NaOH at 40°: O)titration with copper; O)from the reduction in amine nitrogen (van Slyke)

No accessible and sufficiently accurate methods have been reported for the determination of cyclic and linear forms in the products of the polycondensation of esters α-amino acids.

Determination of the cyclic forms by Gavrilov and Balabukha's ionophoresis method [1] gives satisfactory results, but is associated with great experimental difficulties. Moreover, ionophoresis can be applied only to water-soluble polycondensation products. The method of sublimation [2, 3] from the mixture of piperazinediones and polypeptides in a vacuum at high temperature (10^{-3} mm; 140-150°) has an important defect in that part of the peptides undergo thermal degradation under these conditions with formation of a certain amount of piperazinediones [2].

When entering upon a study of the mechanism of the polycondensation of esters of α-amino acids, we were faced with the necessity of developing a simpler and sufficiently accurate method for the quantitative estimation of cyclic forms. We decided to examine a method based on the known action of alkali on piperazinediones, which are broken down with formation of dipeptides [4].

The absence of free amino acids among the substances formed in the earlier stages of the degradation of piperazinediones may be associated with nonequivalence of the peptide linkages in this compound. We studied the degradation of piperazinedione under various conditions of alkali concentration and temperature, and on the basis of this work we found the optimum conditions for complete degradation. The quantitative yield of dipeptides in the polycondensation products was determined after destruction of the piperazinediones from the increase in amine nitrogen (van Slyke) and also from the amount of bound copper in the "biuret" dipeptide copper complex (λ_{max}=610 mμ). One of us [5] has shown previously by the method of differential spectrophotometry that the formation of copper complexes in a polypeptide mixture occurs in a definite sequence. As copper is added, at first the complexes of tetrapeptides and still longer polypeptides are formed (λ_{max}=510-515 mμ). The complexes of the tripeptides (λ_{max}=580 mμ) are formed after the complexing of the longer peptides is complete. Finally, the blue dipeptide complexes are formed. An analogous sequence for the binding of copper by the glycine peptides was found by Dobbie and Kermack [6] on the basis of potentiometric and spectrophotometric data. On the basis of these considerations we developed a method of visual titration of the amount of dipeptides bound to copper. The initial point of the titration was the point at which the formation of "red" (tetrapeptide) and "violet" (tripeptide) complexes ceased, and the end point was indicated by the formation of a very fine suspension of copper hydroxide.

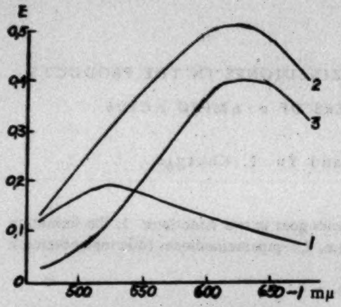


Fig. 2 Absorption spectra of the copper complexes of polycondensation products obtained from the ethyl ester of DL-alanine: 1) at transition point; 2) after the completion of complex formation; 3) absorption spectrum of copper complexes formed after the transition point.

For the determination of the content of piperazinediones, hydrolysis in 0.1 N NaOH at 40° for one hour was used. Under these conditions the piperazinediones were completely degraded to dipeptides, whereas the dipeptides were not affected. In one hour the hydrolysis of 2,5-piperazinedione was almost complete (Fig. 1). The limiting amount of bound copper corresponded to 98% of the theoretical amount for the complete decomposition of piperazinedione. Simultaneously, the extent of the hydrolysis, under the same conditions, of 2,5-piperazinedione was determined by the increase in amine nitrogen, measured by the van Slyke method. The results of the two methods were in close accord. No free glycine, and no piperazinedione, could be detected in the hydrolyzate. Under the given conditions of alkaline hydrolysis (and also in the presence of piperazinediones) diglycine, triglycine, and tetraglycine are stable and do not give rise to an increase in amine nitrogen. On the basis of these preliminary results we carried out the hydrolysis of the piperazinediones present in the polycondensation products obtained from the ethyl esters of glycine and DL-alanine. In the titration of the polycondensation products obtained from the ethyl ester of glycine with 0.4N $CuSO_4$, the interval from point of transition to the blue color to completion of complex formation corresponded to 10.4 ± 0.2% piperazinedione. A parallel determination by the increase in amine nitrogen gave a piperazinedione content of 8.8%. Similar piperazinedione determinations on polycondensation products obtained from the ethyl ester of DL-alanine gave 62.8 ± ± 0.2% by the copper method and 59.8% by the van Slyke method. The piperazinedione content of the polycondensation products obtained from the ethyl ester of DL-alanine has been previously determined [7] by the ionophoretic method, which is possible on account of the good solubility of these products, and a value of 68% was found.

Distillation at 140° and 10^{-3}mm gave a value of 70% for the content of piperazinedione. This value may be too high owing to the thermal degradation of linear polymers with formation of cyclic dimers. In ionophoresis, on the other hand, complete separation did not occur, since a part of the polymers did not pass to the cathode.

In order to check the accuracy of the determination of the transition point in the copper titration, the absorption spectra of copper "biuret" complexes were determined for the polycondensation products obtained from the ester of DL-alanine (Fig. 2). Curve 1 was determined at the "transition point", and the position of the maximum (λ_{max} = =530 mμ) corresponds to the copper complexes of tetrapeptides and still higher polypeptides. The form of the curve at wavelengths of greater than 550 mμ indicates that a small amount of tripeptides may be present. The absorption spectrum of the copper complexes formed after the transition point (Curve 3), i.e. the differences in optical density measured after the completion of complex formation (Curve 2) and at the transition point, corresponds to the absorption due to the copper complexes of dipeptides (λ_{max}=620 mμ). This confirms that in the titration with copper salt the transition point can be determined visually with sufficient accuracy.

It must be pointed out that the titration of dipeptides with a copper salt is difficult when an appreciable amount of tripeptides is present, because the colors given by di-and tri-peptides are visually similar. However, this difficulty can be removed by the use of spectrophotometric titration.

SUMMARY

1. A new method is proposed for the quantitative determination of piperazinediones in presence of peptides from the amount of dipeptides formed by alkaline hydrolysis. Titration with a copper salt and measurement of the increase in amine nitrogen give agreeing results.

2. The piperazinedione contents of the polycondensation products obtained from the ethyl ester of glycine and from the ethyl ester of DL-alanine are determined, the values obtained being 10% and 61%, respectively.

Received May 6, 1955

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

LITERATURE CITED

[1] N. I. Gavrilov and V. S. Balabukha-Poptsova, Bull. Moscow State Univ. No. 1, 105 (1948).

[2] K. Kempf, J. prak. Chem. 78, 243, 258 (1908).

[3] M. Frenkel, E. Katchalsky. J. Am. Chem. Soc. 65, 1670 (1943).

[4] E. Fisher, Ber. 38, 607 (1905); N. D. Zelinsky, Biochem. Z. 141, 97 (1923).

[5] K. T. Poroshin, in the Collection "Investigations in the Field of Macromolecular Compounds", Acad. Sci. USSR Press, 1949, p. 193.

[6] H. Dobbie, W. O. Kermack, Biochem. J. 59, 257 (1955).

[7] V. V. Korshak, K. T. Poroshin, and T. D. Kozarenko, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No. 4, 663. (T.p. 565)*

---

* T.p. = C. B. Translation pagination.

BLANK
PAGE

CURRENT EVENTS

GENERAL MEETING OF THE DIVISION OF CHEMICAL SCIENCES OF THE ACADEMY OF SCIENCES OF THE USSR

At a session of a general meeting of the Division of Chemical Sciences of the Academy of Sciences of the USSR which was held under the chairmanship of Academician M. M. Dubinin on March 30 and 31, 1955, papers were read by Academician A. A. Balandin on "The Present State of the Catalysis Problem and the Theoretical Basis of the Search for Catalysts" *, by Corr. Memb. Acad. Sci. USSR A. D. Petrov on "The Synthesis of Branched Aliphatic Hydrocarbons via 2-Alkenyl Halides" **, and by Corr. Memb. Acad. Sci. USSR A. P. Terentyev on "A New Nomenclature for Condensed Organic Systems".

Opening the discussion on the first paper, Academician M. M. Dubinin emphasized the need to consider the possible directions that future theoretical and experimental investigations may take and to indicate which of these it is most desirable to follow.

In the further discussion on this paper, Ya. T. Eidus, Doc. Chem. Sci. (Institute of Organic Chemistry of the USSR Academy of Sciences), pointed out the relationship existing between the practical problem of the rational, scientific selection of catalysts and the level reached by the theory of catalysis. Eidus considers that, owing to its sound and wide physicochemical basis, the multiplet theory forms a unifying center in which the concepts at the basis of other theories of heterogeneous catalysis are reflected in some degree or other. Thus an example of the relationship between the multiplet theory, the supersaturation theory, and Taylor's nonuniform-surface theory is revealed when we consider the effect of the micro-roughness of a catalyst surface on its activity.

The theory of active assemblages, which identifies the active sites of the catalyst with an amorphous phase, ascribes the activity to a group of atoms – the active assemblage – which corresponds in some measure to a multiplet.

The relationship between the multiplet theory and the intermediate-compound theory finds expression in the nature of the intermediate multiplet complex, in which the basic idea of the intermediate-compound theory is contained. As regards Polanyi's theory, which appeared shortly after the multiplet theory, it is extremely close to the latter and is identical with it in its basic ideas. The multiplet theory is closely related also with the theory of activated adsorption.

Of particular importance is the establishment of a relationship between the multiplet theory and the theory of the transition state. The common feature, fundamental for this relationship, is the assumption of the existence of intermediate states, described as multiplet or activated complexes; the models representing these are often identical, as in both cases configurations formed by two or more atoms of the catalyst are active.

These relationships between various theories and the multiplet theory, the alpha and omega of which is the concept of geometric and energetic correspondence between the reacting species and the catalyst, create, according to A. A. Balandin, the possibility of unifying most of the existing theories into a single one – continued Ya. T. Eidus – and the various views will find their definite places in it. In fact, the specificity of the individual theories arises from the fact that they make different approaches to the same phenomenon, so that they can supplement one another. However, difficulties arise in the unification of theories when the specificity results from the fact that the given theory specializes on phenomena from different fields of catalysis.

Ya. T. Eidus considered some forms of catalysis that occupy an intermediate place between heterogeneous and homogeneous catalysis. Some of these forms of catalysis are well known, for example the hetero-homogeneous reactions such as that of Polyakov, Semenov, and Kovalsky, in which the active center, which is formed at the surface, may be thrown out into the space, where it may initiate a homogeneous reaction; another example is afforded by the homogeneous reactions occurring in liquid films on the surface of a heterogeneous catalyst (Semenov, Chirkov, and Goldansky).

---

* A. A. Balandin's paper is to be found on p. 557 of this translation.

** A. D. Petrov's paper is to be found on p. 571 of this translation.

Ya. T. Eidus stated that he had recently turned his attention to a catalytic phenomenon in which one of the main requirements of the multiplet theory – the activation of all of the original reaction components by the catalyst – was not met, activation by the catalyst surface being confined, for example, to only one of two components. This interesting phenomenon was observed in the iso-synthesis reaction and consisted in the hydrogenation of carbon monoxide with hydrogen over catalysts that were unable to activate hydrogen, for example the classical dehydration catalysts, such as alumina and thoria. As the result of such "semicontact" hydrogenation at high temperatures and pressures, branched hydrocarbons are formed. In Eidus's opinion, a reaction mechanism of this sort is unique and does not correspond to true heterogeneous catalysis; it can be regarded as a special case of heterogeneous catalysis in the sense that in its mechanics rest is not regarded as the opposite of movement, but as a special case of movement characterized by zero velocity. This semicontact mechanism is a special case of a multiplet reaction in which the adsorptions are zero.

Ya. T. Eidus expressed the hope that the theory would reveal the characteristics of such examples of semicontact catalysis, since this may be of significance in the development of the principles underlying the scientific selection of catalysts. A theoretical examination of reactions proceeded by a semicontact mechanism indicates that they should be characterized by activation energies higher than those to be expected if true contact catalysis occured. The same conclusion was reached also by Eyring.

In conclusion, Ya. T. Eidus pointed out that great progress had been made recently in the prediction of the selectivity of a given catalyst in the reactions of functional groups, but the finer points – promoting and activation, sensitivity to slight changes in the method of preparing catalysts, and others – have not yet found their rightful places in the theory of the scientific selection of catalysts.

In joining the discussion, M. I. Temkin (L. Ya. Karpov Physicochemical Institute) remarked that A. A. Balandin was the first to raise, in its general form, the question of the so-called energetic correspondence in catalysis, i.e. the question of how it is possible to select a catalyst for a given reaction on the basis of the values of the energies of the bonds formed by atoms with the catalyst. This is undoubtedly a very interesting question, for although data on bond energies are at present inadequate, they may be obtained in the future, and if it should be posible to select catalysts on the basis of these data, work on catalysis would be greatly assisted.

At a first glance it would appear – continued M. I. Temkin – that it would be impossible to do this, because reaction rates cannot be expressed unequivocally by quantities of a thermodynamical nature, such as bond energies. It is known, however, that there is a definite type of correspondence between kinetic and energetic quantities, an example of which is provided by the well known relationships in the field of acid catalysis. In principle, this justifies the posing of this question.

In addition to kinetic methods of determining the energies of bonds between atoms and the surface, it is possible to find methods that are more direct. In the Chemical Kinetics Laboratory of the Karpov Institute the study of chemical equilibria has been recently applied for this purpose, the participants in these equilibria being gaseous components, on the one hand, and surface compounds, on the other.

The equilibrium data – stated M. I. Temkin – enable the bond energies to be determined for the surface compounds. N. V. Kulkova has investigated the energies of the bonds formed by oxygen with the surfaces of various kinds of oxidative catalysts. The results of such measurements can be used for the experimental elucidation of the problem of energetic correspondence.

From the theoretical point of view it is possible to approach this problem in a way that is somewhat different from that adopted in A. A. Balandin's work, that is to say we can examine in a fairly general way the problem of a heterogeneous catalytic process composed of two stages (in general, apparently, every catalytic process must consist of stages, so that two is the least possible number). If we write down the equation for the rate of the process that corresponds to stationary-state conditions, and then, in determining the rate constants for each stage, assume the same relationship between kinetic and thermodynamical characteristics as that found for acid catalysis, we may solve the question, in its general form, of which catalyst will give the maximum reaction rate. M. I. Temkin has carried out such a treatment on the assumption that the change in activation energy from one catalyst to another is one-half of the change in the bond energy in the intermediate surface compound (this is in accord with the results that he obtained in experimental studies of the synthesis of ammonia and other reactions). It is then found that maximum reaction rate is attained when one-half of the surface is covered with the intermediate compound. Temkin distinguishes two cases. In the first, one stage attains equilibrium before the reaction as a whole does. This occurs, for example, in the synthesis of ammonia. The required half coverage can then be expressed in terms of the thermodynamical characteristics of the equilibrium stage. In this way the problem is completely solved.

In the second case, which corresponds to that examined by A. A. Balandin, the reaction occurs under conditions far removed from equilibrium. By the approach that we have made it is now impossible to express, in a general form, the conditions for half coverage in terms of bond energies. This can be done, however, if it is assumed that the relationship between equilibrium and rate constants is valid not only for each stage separately, but also for the two stages in association. This assumption is rational when the first and second stages are analogous processes, as occurs, for example, in the doublet scheme applied by A. A. Balandin. Such reactions can be termed symmetrical. The most symmetrical reactions in this sense are isotope-exchange reactions. For the case considered by Balandin the same result is obtained by this method as that obtained by him with the aid of volcanolike curves: it is found that the sum of the energies of the bonds formed with the surface should be equal to one-half of the sum of the energies of the bonds that were broken and of the bonds that are formed.

In conclusion, M. I. Tamkin said that, although it is impossible to select the optimum catalyst on the basis of bond energies in the general case, it can be done (if the above assumptions are valid) in two important special cases: reactions in the vicinity of equilibrium, and symmetrical reactions.

In entering the discussion on the paper, Corr. Memb. Acad. Sci. USSR S. Z. Roginsky pointed out that this concentration of effort on working out the scientific principles of the selection of catalysts was very timely, but rapid progress must not be expected, for the problem is a very difficult one which has not been even partially solved, neither here nor abroad. At the same time, the theory of the selection of catalysts has given rise to some interesting concepts, and the experimental material that has been accumulated gives us reason to hope for success if we make a serious collective effort over a long period. In his paper A. A. Balandin correctly emphasized — stated S. Z. Roginsky — that the model concepts of his selection theory and the equations to which they give rise, although they apply to an extensive range of reactions, are not by any means universal and must be applied to definite types of reactions. Roginsky pointed out further that in his own investigations it had been shown that some markedly different types of catalysis mechanism existed. This fact must be taken into account in the development of a selection theory, since the laws are different for different types. For heterogeneous catalysis it has been shown that there are a few basic kinds of activation effect produced by the catalyst on the reaction. In organic catalysis one of the most common of these is acid-base activation. A solid catalyst very often acts as a solid acid and base by the same mechanism of proton transfer as that found in liquid acids and bases (and also, much more rarely, in aprotonic acids). The use of solid surfaces as acid-base catalysts introduces some essentially new features.

On the surface there may exist simultaneously, and as immediate neighbors, sites having acidic and basic properties. S. Z. Roginsky pointed out that acids and bases may be obtained which surpass in strength the strongest acids and bases met in homogeneous media, that centers differing in acidity and basicity may be found on the surface and different geometric dispositions of these centers may occur, and that both the arrangement of the centers and their acid and basis properties may vary over a wide range for different catalysts, in presence of various additives, and for different methods of preparing the catalyst.

Catalysts act — continued S. Z. Roginsky — by a second type of mechanism based on electron transitions, which is just as common, but has no exact analogs in homogeneous catalysis. Whereas in acid-base catalysis the catalyst generally initiates the process by removing a proton from a substrate molecule or transferring a proton to it, in oxidation-reduction or electronic catalysis the typical initiating act of activation is the transfer of an electron to the substrate or the drawing of an electron from the substrate into the solid. Other types of catalytic action also exist.

In Roginsky's opinion it is very important to distinguish clearly the most common fundamental types of primary process of substrate activation by the catalyst, establish definite gradations and sequences among these with respect to the forces of interaction between the catalyst and the substrate, and then control this interaction in order to obtain the desired effect.

In the field of selection theory — said S. Z. Roginsky — we are already in a position to predict which catalysts will be active for the acceleration of processes of low specificity. But an extremely difficult and important problem remains — a rational approach to the selection of specific catalysts. A. A. Balandin's paper shows that a successful approach to the solution of this problem can be made on the basis of the theory of multiplets. The application of electronic concepts hold out great promise in this field. An important part should be played in the discovery of the laws of selection by the periodic system of elements, for, in particular, the acid-base and electronic properties of substances, of which we have already spoken, i.e. the power of acting as acceptors and donors of protons and electrons, vary with changes in the elementary composition of the compounds. Basic properties become more pronounced as the atomic weight is increased and as we move from right to left in Mendeleev's periodic table; acidic properties behave similarly as we move from left to right. For a given element basic character increases as the valency falls. In the electronic properties a determining part is played by the presence of unoccupied places in the d electron shells and the number of such places. The first simple relationships for the effect of the combination of elements on their electronic properties, etc., have been found. S. Z. Roginsky considers that, if our approach to the periodic system is sufficiently profound and we make investigations under comparable conditions, the system will provide very rich and valuable material in this field, the obtaining of which is of special importance in that a large number of "blank places" remain in the periodic system with respect to the study of the catalytic properties of the elements and their compounds.

It is necessary also to take into account the possibility of exerting an extremely close control over the catalytic properties of a solid by making small additions of a definite type.

As an example, Roginsky cited the semiconductor catalyst, nickelous oxide. If 0.05-0.1% of lithium oxide is introduced into the nickelous oxide lattice (it goes into solid solution), the catalytic properties are greatly changed; in particular, the activation energy changes. The introduction of lithium increases the number of electron holes in the lattice, and this had a detrimental effect on the catalytic properties. On the other hand, the introduction of large amounts of magnesium oxide into the lattice, where it forms a solid solution, has almost no effect on the activity; here the cation has the same charge as Ni^{++} and is not able to change its charge. According to the literature, the introduction of small amounts of iron, indium, chromium, and some other tervalent elements greatly affects the conductivity, and also greatly alters the catalytic functions, their effects being in the opposite direction to that of lithium. The activity can therefore be controlled within wide limits in a rational fashion.

When a solid acts as a catalyst of the acid-base type, activation can be effected by other additions, which in combination with the catalyst give acids or bases of enhanced strength.

We stand — stated S. Z. Roginsky — at the very beginning of a great collective task — the search for scientific principles that can form the basis of the selection of catalysts. Important scientific forces have been mobilized for the solution of this problem and the creative efforts of a number of scientific teams have been concentrated on it, and this action must be regarded as correct and rational. There is reason to hope that in a few years there will be a substantial increase in the amount of reliable experimental material, accompanied by the discovery of new catalysts and considerable progress in work on the search for the scientific principles of the selection of catalysts.

G. K. Boreskov, Doc. Chem. Sci. (Karpov Physicochemical Institute), pointed out that with respect to a limited number of reactions the solution of the problem would greatly contribute to the progress of the chemical industry. This problem was an extremely difficult one, however, and the gap between the requirements of practice and the possibilities of theory were very great indeed.

For cases in which the reacting substances and the catalyst form a single active complex, A. A. Balandin has shown by his multiplet theory that by evaluating the energy of formation of this complex and considering its further transformations we may predict the activation energy for the chemical reaction in presence of the given catalyst.

It should be noted, however — stated G. K. Boreskov — that quantitative calculations, even approximate ones, come up against considerable difficulties. The least reliable calculation is that of the energies of the bonds formed by individual atoms of the reactants with the catalyst. It is difficult to understand how it is possible to evaluate these bond energies from energies of formation of the corresponding compounds in a phase.

If I have understood A. A. Balandin correctly — said G. K. Boreskov — then in the table in which data are given for various catalysts the energies of the bonds formed with the catalysts were calculated from the experimentally determined activation energies for the dehydrogenation of hydrocarbons and the dehydration and dehydrogenation of alcohols. Though it may be possible to understand that for the dehydrogenation of hydrocarbons we may determine the energy of the bond formed by hydrogen with the catalyst, it is very difficult to imagine how the energy of the bond formed by oxygen with the catalyst can be determined for the dehydration of an alcohol. In Boreskov's opinion, this last quantity has no direct bearing on the dehydration reaction, and the approximations that have to be made in the proposed scheme of calculation make it difficult to apply it in the solution of practical problems associated with the selection of catalysts. Results of greater reliability can be expected from the application of the theory to the estimation of the relative rates of various reactions over a given catalyst, as given in the paper.

G. K. Boreskov discussed briefly the aspects of the problem (the scientific principles of the selection of catalysts) that were being examined in the Technical Catalysis Laboratory of the Karpov Institute on the basis of the view that the action of solid catalysts is determined by intermediate surface chemical interaction between the reactants and the catalyst.

Previous work by G. K. Boreskov has shown that the activity per unit area of catalyst (specific catalytic activity) for various metal and oxide catalysts is approximately constant.

Hence, the main factor determining specific catalytic activity is the chemical composition. This fact determines the problems which, in Boreskov's opinion, will have to be solved in order to create a theory of catalyst selection.

The first, immediate problem is the discovery of the general laws relating specific catalytic activity with the chemical composition of the catalyst and, as S. Z. Roginsky had pointed out, the search for these laws is best carried out with the aid of Mendeleev's periodic law, which provides the most complete generalization of chemical properties.

Working in this direction, G. K. Boreskov has obtained some results on the specific catalytic activity of metals in oxidation, hydrogenation, isotope-exchange, and other reactions. It was found that, for reactions in which the activation of hydrogen occurred, the specific catalytic activities of metals in given periods of Mendeleev's system increased at first, attained a maximum when the d zone was almost filled with electrons, i.e. for Ni, Pd, and Pt, and then fell sharply to the succeeding metals of Group I B. On the other hand, for the synthesis of ammonia, which is associated with the activation of molecular nitrogen, maximum specific activity was found for Fe, Ru, and Os, i.e. corresponded to the greatest deficiency of electrons in the d zone. Within individual groups, the specific catalytic activity increased with increase in atomic number.

Relationships of this sort are of definite interest for the selection of catalysts, and they are bound to cover various classes of chemical compounds (oxides, sulfides, nitrides, etc.). Great possibilities are opened by the investigation of alloys, the use of which permits finer control over electron structure.

Secondly, we must try to discover the laws of the formation of intermediate surface compounds between the reacting substances and the catalyst and must study the properties of these compounds. In Boreskov's opinion, much may be attained in this direction by the use of labeled atoms, since they enable the reactivity of the surface compound to be determined without affecting the composition of the catalyst under investigation.

The third direction of work is concerned with the selection of catalysts for complex reactions occurring in presence of multicomponent catalysts. In this case individual stages may be effected on different parts of the catalyst, and the way in which these are combined in the catalyst and the ratios of their surfaces may affect the selectivity of the process within wide limits.

Apart from these questions — continued G. K. Boreskov — we must pay great attention to matters relating to the creation of a definite internal surface and porous structure within the catalyst. There can be no doubt that adequate development of the theories underlying the search for and the selection of catalysts can be brought about only by approaching the problem from every side and examining it from different points of view. It is quite right, therefore, that in the attack on this problem we should bring to bear the efforts of a wide circle of investigators who are themselves developing various theoretical concepts in the field of catalysis. However, the unification of the efforts of various schools of thought must proceed not with an accompanying happy coexistence of various theories, but to the accompaniment of a conflict of opinions. Only in this way can a sound general theory be created and our task completed.

V. V. Voevodsky, Doc. Chem. Sci. (Institute of Chemical Physics of the USSR Academy of Sciences), discussed investigations directed to the development of the chain theory of heterogeneous catalysis. The basis of this theory is the assumption that in most cases rapid surface reactions are brought about by the aid of geometrically localized active intermediate compounds, the fundamental property of which is their ability to react very quickly with low activation energy with molecules of the original substances.

The concept of the existence of free radicals on the surface of heterogeneous catalysts cannot be regarded as original, it has existed in the literature for several decades. The new feature in the theory developed by V. V. Voevodsky was the assumption of the possibility of the formation of surface chains, i.e. the possibility of a process in which, as a result of the indestructibility of the free valency in the reaction of a radical with a molecule, each act of reaction leads to the regeneration of the free radical, so that after the first act, in which a free radical is produced, a large number of further acts may be brought about, resulting in a chain of elementary acts and its propagation.

The application of chain concepts in heterogeneous catalysis is of interest, in Voevodsky's opinion, mainly because it opens up wide possibilities for the use of the theoretical ideas and methods of investigation created and developed in the course of the evolution of the chain theory of homogeneous reactions, for the study of the mechanisms of heterogeneous processes and for the discovery of methods of controlling these processes.

What inferences can already be drawn concerning the mechanism of catalysis from the general postulates of the chain theory? The most interesting is the conclusion that a catalyst has two functions. If the heterogeneous process has a chain character, then as in any other chain process, in an analysis of its course we must take into account the factors having a substantial effect on the initiation and breaking of chains, on the one hand, and on processes of chain propagation, on the other.

Just as in homogeneous chain reactions, the acts of initiation and breaking of chains determine the concentration of radicals, i.e. the rate of the process, but chain-propagation reactions determine the identity of the products, i.e. the direction of the process.

In heterogeneous catalysis it is, of course, to be expected that the rates of all these elementary stages will depend very greatly on the properties of the catalyst.

Hence, in the chain theory, matters relating to the rate and the direction (selectivity) of the catalytic process are clearly separated from one another, and the possibility arises of controlling the processes in these respects, taken separately. In fact — said V. V. Voevodsky — if we have two catalysts, and on one of these chains are readily initiated but the propagation of the chains goes with great difficulty whereas on the other chain-propagation reactions are rapid but initiation occurs with difficulty, then the improvement of the catalytic properties of these two catalysts must be effected by quite different methods. In the first case, additions must be made which will encourage reaction between surface radicals and molecules, and in the second, some way must be found to facilitate the reactions in which radicals are formed, i.e. the dissociation reactions of the original molecules at the surface.

These general postulates must be made to serve as the basis of experimental investigations, in the course of which it is our intention to verify the possibility of applying chain concepts in heterogeneous catalysis.

The main ways in which this theory can be experimentally verified, as proposed in a very general form in papers by N. N. Semenov, F. F. Volkenshtein, and V. V. Voevodsky, can be formed into a plan which falls into three parts:

1. Determination of the structures and properties of the active intermediate compounds, local active centers, or, as they have been called, surface radicals. The solution of this problem lies mainly in the application of modern physical methods of investigation.

2. Determination of the chain length. The experiments must consist in the measurement of the number of molecules of products formed for each originally created surface radical, i.e. in the measurement of a peculiar "catalytic" or "radical" yield. If such experiments lead to an unequivocal result, then the occurrence of chain reactions on solid surfaces can be regarded as proved and the question will arise of the extent to which such processes occur.

3. The performance of large number of detailed investigations into the kinetics of various heterogeneous processes. The results in themselves will not be able to provide unequivocal indications of the mechanism of the process, but, in Voevodsky's opinion, in combination with data obtained by the first two methods they may be extremely valuable for the understanding of the nature of the process and for the development of rational methods of controlling it.

In a short address, Academician A. N. Terenin considered matters relating to the investigation of the molecular structures of catalysts, in particular the use for this purpose of modem methods of infrared spectroscopy, paramagnetic resonance, etc.

Summarizing the discussion on Academician A. A. Balandin's paper, the chairman, Academician M. M. Dubinin pointed out the necessity of planning future theoretical and experimental investigations on the catalysis problem, and he called for united efforts by the various schools with the object of solving this problem. The Scientific Council on the Catalysis Problem, which has been instituted by the Division of Chemical Sciences of the USSR Academy of Sciences and which includes scientists of the Academy of Sciences, industrial institutes, and higher teaching establishments, was called upon to play a dominant part in this matter and to bring about the very necessary coordination of all the investigations being carried out in this field.

Various aspects of the interesting work reported in a paper by Corr. Memb. Acad. Sci. USSR A. D. Petrov at the general meeting of the Division were discussed by Corr. Memb. Acad. Sci. USSR A. P. Terentyev, Prof. P. G. Sergeev, Academician M. M. Dubinin, Prof. K. I. Ivanov, and others.

The paper by Corr. Memb. Acad. Sci. USSR A. P. Terentyev was discussed by Prof. P. G. Sergeev, Acad. I. L. Knunyants, Corr. Memb. Acad. Sci. USSR D. N. Kursanov, and others. In concluding the discussion, Academician M. M. Dubinin pointed out the value of the new system of nomenclature worked out by Corr. Memb. A. P. Terentyev and his coworkers, and he stated that in its relation to the coming discussion of problems of chemical nomenclature at the Fourteenth Congress of the International Union of Pure and Applied Chemistry in Zurich the work carried out in this direction in the Soviet Union would acquire even greater significance.

BLANK
PAGE

SYSTEMS CONTAINING HYDROGEN PEROXIDE AT HIGH CONCENTRATION

COMMUNICATION 10. THERMAL STABILITY OF UREA PERHYDRATE

S. Z. Makarov and B. A. Lebedev

In an investigation of the ternary system $CO(NH_2)_2 - H_2O_2 - H_2O$ by the solubility method [1], the conditions were found for the formation in this system of the compound $CO(NH_2)_2 \cdot H_2O_2$, urea perhydrate, known in industry under the name of Hyperol. The compound synthesized was carefully purified and has now been subjected to thermal analysis and investigated systematically in order to determine its stability at various temperatures.

EXPERIMENTAL

The heating curves were determined over the temperature range 20–150° with a Kurnakov recording pyrometer having a differential thermocouple. The curves obtained for the heating of urea (Fig. 1) are characterized by a single endothermic effect at 132–133°, which corresponds to melting.

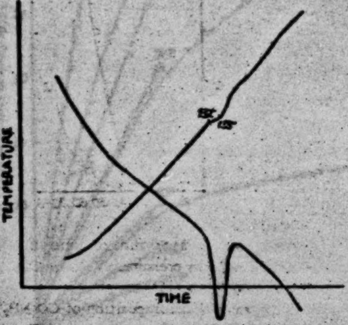


Fig. 1

The form of the heating curve of $CO(NH_2)_2 \cdot H_2O_2$ is quite different. At 64° urea perhydrate begins to decompose, and at 67° the process is accompanied by a marked exothermic effect. As a result of the heat evolved in the decomposition of the H_2O_2 eliminated, the temperature of the sample rises rapidly to 110° (Fig. 2). The differential heating curves for the compound $CO(NH_2)_2 \cdot H_2O_2$ are quite analogous in form to curves that we have given in previous papers for the thermal decomposition of perhydrate compounds. The heating curves that we have obtained confirm the presence of H_2O_2 chemically bound to $CO(NH_2)_2$ in the compound $CO(NH_2)_2 \cdot H_2O_2$.

Thermal Stability of $CO(NH_2)_2 \cdot H_2O_2$. The investigation of the thermal stability of $CO(NH_2)_2 \cdot H_2O_2$ is of practical interest, for this compound is one of the few perhydrate compounds of industrial importance. As is well known, urea perhydrate is readily souble in water and its H_2O_2 content is about the same as that of perhydrol (30% hydrogen peroxide); it is widely used for medical and cosmetic purposes.

The thermal stability of $CO(NH_2)_2 \cdot H_2O_2$ has not been given adequate attention in the literature, except in a paper by Jänecke [2], who gives an upper stability limit of 85°, without any indication of the method by which this value was obtained. When hermetically sealed under ordinary conditions the compound $CO(NH_2)_2 \cdot H_2O_2$ is a fairly stable substance, but when the temperature is raised to 40° and higher the stability falls appreciably and continuous decomposition sets in with evolution of oxygen.

The stability of $CO(NH_2)_2 \cdot H_2O_2$ was investigated in the laboratory under isothermal conditions over the temperature range 45–70° and at presssures of 760 and 20 mm, several parallel experiments being carried out for times up to 60 hours. The weights of the samples fell in a regular manner, owing to the loss of oxygen and water; the loss was calculated as a percentage on the weight of the sample (0.3–1.6 g).

The results of investigations at 55°, 60°, 65°, and 70° (760 mm) and at 40°, 45°, 50°, 55°, and 60°, (20 mm) on the thermal stability of $CO(NH_2)_2 \cdot H_2O_2$ are given in the table and are shown graphically in Fig. 3. The decomposition curves for 760 mm and the temperatures indicated are almost linear for times up to 20 hours. On the other hand, the decomposition curves obtained at a residual pressure of 20 mm have appreciable curvatures, and at 40° and 45° the process tends to slacken off gradually. Above 50° (20 mm) decomposition is very vigorous: the

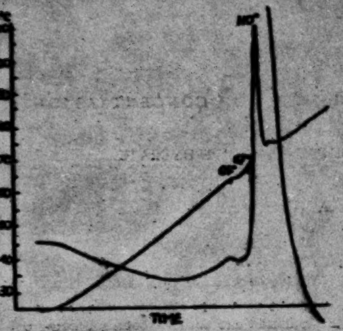


Fig. 2

decomposition curves are slightly curved, but are almost linear at first. The effect of reduced pressure is considerable, but its effect is mainly associated not with loss of active oxygen, but with removal of hydrogen peroxide and water formed in the decomposition.

An examination of the total loss (as a percentage of the amount of $CO(NH_2)_2 \cdot H_2O_2$ originally taken) indicates that reduction in pressure from 760 mm to 20 mm is similar in effect to a rise in temperature of about 25°. At both pressures increase in temperature is accompanied by more intensive decomposition of $CO(NH_2)_2 \cdot H_2O_2$ (increase in the slope of the curve).

An examination of the mean rate of overall decomposition of $CO(NH_2)_2 \cdot H_2O_2$ in the first stage of the process, in which the curves are almost linear, indicates, as the graphical representation in Fig. 4 shows, that there is a rapid decrease in the rate of decomposition of $CO(NH_2)_2 \cdot H_2O_2$ as the temperature falls, particularly at the lower pressure, 20 mm. We may suppose tentatively that the compound $CO(NH_2)_2 \cdot H_2O_2$ will have adequate stability below 30°. Observations on samples of $CO(NH_2)_2 \cdot H_2O_2$ that have been kept at room temperature confirm this supposition.

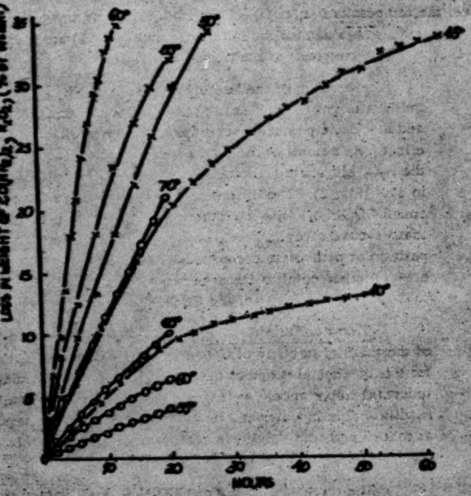


Fig. 3. x) 20 mm pressure; o) 760 mm pressure.

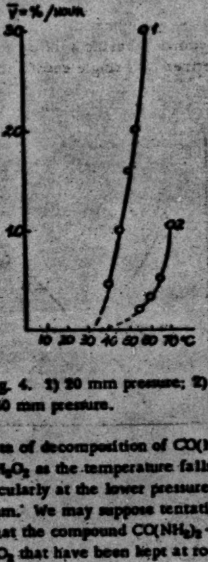


Fig. 4. 1) 20 mm pressure; 2) 760 mm pressure.

DISCUSSION OF RESULTS

The process of thermal decomposition of urea perhydrate, as can be seen from an examination of the thermal curve (Fig. 2), is evidently associated with the elimination of an H_2O_2 molecule and its decomposition into H_2O and O_2 in accordance with the equations:

$$CO(NH_2)_2 \cdot H_2O_2 \rightarrow CO(NH_2)_2 + H_2O_2$$

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}\ O_2 \text{ exothermic reaction}$$

$$CO(NH_2)_2 \cdot H_2O_2 \rightarrow CO(NH_2)_2 + H_2O + \frac{1}{2}\ O_2 \text{ overall reaction}$$

The rate of formation of carbon monoxide can be calculated by two independent means: 1) graphical differentiation of the curve for the accumulation of carbon monoxide (Curve 2), and 2) from the specific activity of formaldehyde and the rate of change with time of the actual activity I_{CO} of carbon monoxide.

If, in fact, the carbon monoxide is formed exclusively from formaldehyde, the change in the actual activity of carbon monoxide in unit time must be equal to the rate of formation of carbon monoxide multiplied by the specific activity of formaldehyde.

Thus

$$\frac{dI_{CO}}{dt} = a_{CH_2O} \cdot w_{CO},$$

so that

$$w_{CO} = \frac{1}{a_{CH_2O}} \cdot \frac{dI_{CO}}{dt}. \qquad (2)$$

TABLE 1

Variation of the Concentrations and Actual Activities of Formaldehyde and Carbon Monoxide with the Time spent by the Reaction Mixture in the Reaction Zone at 670°. (Specific activity of labeled formaldehyde a_{CH_2O} = = 0.5 microcurie/mmole, actual activity $I_{CH_2O} = 1550 \cdot 10^{-5}$ microcurie/liter)

Time of contact (seconds)	Amount of CH_2O supplied (mmole/liter)	Concentration of CH_2O (mmole/liter)	Concentration of CO (mmole/liter)	Actual activity of CH_2O, I_{CH_2O} ($\times 10^{-5}$ microcurie/liter)	Actual activity of CO, I_{CO} ($\times 10^{-5}$ microcurie/liter)	Total activity $I = I_{CH_2O} + I_{CO}$	Departure from amount supplied (%)
0.021	0.024	0.094	0.22	–	–	–	–
0.024	0.031	0.110	0.24	1210	282	1492	– 4
0.039	0.024	0.187	0.22	–	–	–	
0.043	0.031	0.174	0.34	987	803	1793	+15
0.056	0.036	0.231	0.32	660	915	1573	+ 1.4
0.074	0.026	0.290	0.53	–	–	–	
0.077	0.044	0.300	0.54	408	1300	1708	+10
0.083	0.031	0.281	0.60	308	1625	1933	+25
0.091	0.023	0.330	0.66	–	–	–	
0.127	0.041	0.386	1.20	53	1655	1697*	
0.180	0.027	0.350	1.53	–	–	–	

---

* $I = I_{CH_2O} + I_{CO}$ has only a tentative value since at this point the specific activity of formaldehyde is close to zero.

Table 2 gives rates of consumption of formaldehyde k [CH_2O] and rates of formation of carbon monoxide, calculated graphically by differentiation of the kinetic curve for the accumulation of carbon monoxide, and also by Equation 2. The rate of change of the actual activity of carbon monoxide with time dI_{CO}/dt was calculated by graphical differentiation of the curve expressing the dependence of the actual activity of carbon monoxide on time Fig. 2). As can be seen from Table 2 within the limits of experimental error the rates of consumption of formaldehyde are equal to the rates of formation of carbon monoxide. Hence, this method also leads to the conclusion that the process occurs in the successive stages: methane → formaldehyde → carbon monoxide.

The next stage of this work will be the establishment, with the aid of the kinetic tracer method, of the mechanism by which carbon dioxide is formed, and also of the part taken by methanol in the mechanism of the oxidation of methane, for, as reported in the literature, in the oxidation of methane in presence of a nitrogen oxide catalyst, not only formaldehyde, but also methanol is formed.

Owing to the thermal effect (local overheating, since the decomposition of H_2O_2 takes place with evolution of heat), evolution occurs not only of oxygen, but also of water in an amount that is the greater, the higher the temperature and the lower the residual pressure. In other words, oxygen is evolved and the $CO(NH_2)_2 + H_2O$ remaining undergoes dehydration. If only oxygen was evolved in the process, then the theoretical loss for $CO(NH_2)_2 \cdot H_2O_2$ could not exceed 9.3%, whereas at 65° (760 mm) and at 45°, 50°, or 55°, or 65° (20 mm) the actual losses are higher than this, even in the course of 20 hours. For the complete dehydration of chemically pure $CO(NH_2)_2 \cdot H_2O_2$, however, the total loss of $O_2 + H_2O$ would be 30.1% on the assumption that the completely dry $CO(NH_2)_2$ remains completely unaffected. Actually, however, partial decomposition of the compound $CO(NH_2)_2$ occurs. Nevertheless, at low temperatures (below 20—30°) urea perhydrate decomposes extremely slowly under hermetic conditions, and it may be preserved for a long time, even without the addition of special stabilizers.

TABLE

Thermal Decomposition of $CO(NH_2)_2 \cdot H_2O_2$ (expressed as percentage loss in weight)

Time (hours)	Temperature (°c)							Pressure (mm)	Mean rate of decomposition (percent per hour)
	40	45	50	55	60	65	70		
2				0.46	0.97	1.18	2.66	760	$\bar{v}_{55} = 0.196$
4				0.89	1.81	2.35	4.82	760	$\bar{v}_{60} = 0.322$
6				1.15	2.46	3.40	7.01	760	$\bar{v}_{65} = 0.499$
8				1.65	3.19	4.34	9.07	760	$\bar{v}_{70} = 1.049$
10				2.00	3.74	5.46	11.24	760	
12				2.39	4.29	6.31	13.14	760	
14				2.77	4.88	7.27	14.96	760	
16				3.19	5.38	8.18	16.93	760	
18				3.47	5.86	9.08	18.94	760	
20				3.91	6.45	9.98	20.98	760	
1					3.15			20	$\bar{v}_{40} = 0.450$
3	1.11	3.75	4.67	8.09	9.83			20	$\bar{v}_{45} = 1.00$
6	2.80	7.41	9.82	14.35	20.70			20	$\bar{v}_{50} = 1.60$
9	4.37	10.51	13.24	19.03	29.34			20	$\bar{v}_{55} = 2.00$
12	6.36	13.31	17.82	23.40	33.66			20	$\bar{v}_{60} = 3.00$
15	7.88	15.91	21.90	26.90					
18	8.72	18.37	25.80	29.78					
21	9.50	20.36	29.93	31.81					
24	10.14	22.07	33.11	33.34					
27	10.81	23.51	34.08						
30	11.18	24.80							
33	11.44	26.04							
36	11.82	27.16							
39	12.11	28.00							
42	12.21	28.81							
45	12.57	29.88							
48	12.80	31.00							
51	13.10	31.20							
54		32.50							
57		33.12							
60		33.62							
63		33.76							

SUMMARY

1. Heating curves have been determined for $CO(NH_2)_2$ and $CO(NH_2)_2 \cdot H_2O_2$ and the curve for the latter indicates the presence of a thermal effect at 64-67° associated with the decomposition of urea perhydrate.

2. Investigation of the decomposition of $CO(NH_2)_2 \cdot H_2O_2$ over the temperature range 40-70° and at pressures of 760 and 20 mm shows that increase in temperature and reduction in pressure have considerable effects on the process.

3. The compound $CO(NH_2)_2 \cdot H_2O_2$ is adequately stable below 20-30°.

Received February 23, 1955

N. S. Kurnakov Institute of General and
Inorganic Chemistry of the USSR Academy
of Sciences

LITERATURE CITED

[1] S. Z. Makarov and B. A. Lebedev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, No. 1, 58 (T. P. 51)*.

[2] E. Jänecke, Rec. trav. chim. 51, 579 (1932); E. Jänecke, Z. Electrochem. 36, 674 (1930).

---

* T.p. = C. B. Translation pagination.

BLANK
PAGE

STUDY, WITH THE AID OF LABELED ATOMS, OF THE REACTION MECHANISM OF THE OXIDATION OF METHANE

MECHANISM OF THE FORMATION OF CARBON MONOXIDE

I. N. Antonova, V. A. Kuzmin, R. I. Moshkina, A. B. Nalbandyan,
M. B. Neiman, and G. I. Feklisov

In work on photochemical oxidation of methane sensitized by mercury atoms, Nalbandyan [1] showed that at high temperatures the main reaction products are formaldehyde, carbon monoxide, and carbon dioxide. It was concluded from an analysis of the kinetic curves for the accumulation of these products that a sequence of reactions occurs in which formaldehyde is formed from methane, carbon monoxide from formaldehyde, and carbon dioxide from carbon monoxide, i.e. the occurrence of the following sequence of reactions was proved:

$$CH_4 \xrightarrow{+O_2} CH_2O \xrightarrow{+O_2} CO \xrightarrow{+O_2} CO_2.$$

In view of the importance of these conclusions for the mechanism of the oxidation of methane, the need arose for their verification for the thermal oxidation of methane, for which purpose we applied the new kinetic method developed by Nieman[2] for the study of reaction mechanisms with the aid of labeled atoms.

The present paper gives the results of the investigation of the way in which carbon monoxide is formed. For this purpose a detailed study was made of the kinetics of the accumulation of formaldehyde and carbon monoxide in presence of a small amount of labeled formaldehyde $C^{14}H_2O$, which was added to the reaction mixture of methane and air. The regularities observed in the kinetics of the changes in the specific activities of the formaldehyde and carbon monoxide formed in the course of the reaction enabled us to solve the problem in favor of the formation of carbon monoxide from formaldehyde.

EXPERIMENTAL

Methane was oxidized with atmospheric oxygen. In order to obtain appreciable amounts of intermediate products, a small amount of nitrogen oxides was added to the reaction mixture. The experiments were carried out in a continuous-flow apparatus. The reaction mixture, which contained about 33% of methane, 66% of air, 0.1% NO, 0.5% of carbon monoxide, and 0.07% of labeled formaldehyde ($C^{14}H_2O$), was passed to the reactor, which had been heated to 670°. The labeled formaldehyde was prepared by the incomplete oxidation of labeled methanol over a silver catalyst. The methanol was synthesized from labeled carbon dioxide by the method described by Feklisov [3].

The carbon monoxide was added to the reaction mixture with the object of determining whether the specific activity curves of formaldehyde and carbon monoxide intersect at the point corresponding to the maxium activity of carbon monoxide β_{CO}. In accordance with the theory of this kinetic tracer method, the intersection of the kinetic specific-activity curves of formaldehyde and carbon monoxide at the maximum value of β_{CO} is an unequivocal proof of the occurrence, as a stage in the sequence, of the process

$$CH_2O \xrightarrow{+O_2} CO.$$

Addition of labeled formaldehyde to the reaction mixture was effected by passage of part of the air through a bubbler containing 10% formaldehyde having specific activity of 0.5 microcurie /mmole. In order to prevent the polymerization of the formaldehyde passing on, the tubes connecting the bubbler to the reactor were heated to 100-120°. In order to asorb the formaldehyde gas leaving the reactor, a large absorption tower was used in which water flowed downward over a filling of short glass tubes.

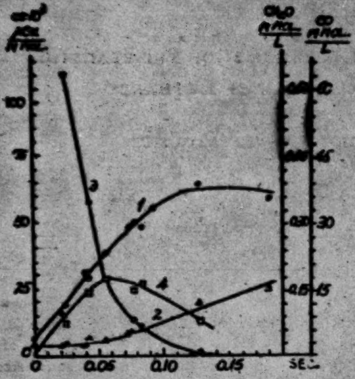


Fig. 1. Kinetics of the accumulation of formaldehyde (Curve 1) and carbon monoxide (curve 2) and the variation of their specific activities α_{CH_2O} (Curve 3) and β_{CO} (Curve 4)

After absorption of formaldehyde, the residual gas was collected in a gas holder. The formaldehyde content of the aqueous solution was determined by the hydroxylamine method. In order to obtain the solid precipitate necessary for the determination of the specific activity of the formaldehyde, it was converted into its 2,4-dinitrophenylhydrazone.

The amount of carbon monoxide and its specific activity were determined after oxidation with iodine pentoxide and absorption of the carbon dioxide formed in baryta water. The resulting precipitate of barium carbonate was centrifuged off, washed with hot water and with alcohol, dried, and weighed. Its specific activity was then determined.

Fig. 1 gives curves for the accumulation of formaldehyde (1) and carbon monoxide (2) as functions of the time spent by the reaction mixture in the reaction zone. It will be seen from Fig. 1 that the formaldehyde concentration increases as the time increases and attains a maximum for a time of 0.12-0.14 second. Further increase in the time results in a slow fall in the formaldehyde concentration. On the other hand, the carbon monoxide concentration rises continuously. The accumulation of carbon monoxide is characterized by the fact that, from the moment that formaldehyde ceases to accumulate, carbon monoxide begins to accumulate at a constant rate. The variations of the specific activities of formaldehyde (α_{CH_2O}) and carbon monoxide (β_{CO}) are represented by Curves 3 and 4 in Fig. 1. All the data and results for these experiments are given in Table 1.

It will be seen from 3 (Fig. 1) that the specific activity of formaldehyde diminishes with increase in time of contact, i. e. with increase in the formaldehyde content of the reacting mixture, whereas the specific activity of carbon monoxide (Curve 4) at first rises with time, and then begins to fall, more slowly, however, than the specific activity of formaldehyde. At the point corresponding to $t = 0.056$ second the curves intersect and β_{CO} becomes equal to α_{CH_2O}.

As stated above, the intersection of the curves for the specific activities of formaldehyde and carbon monoxide in the point corresponding to maximum specific activity of CO is a direct proof of the sequence of processes:

$$CH_4 \longrightarrow CH_2O \xrightarrow{+O_2} CO.$$

An idea of the mechanism of the formation of carbon monoxide can be formed also from a comparison of the rate at which formaldehyde is consumed with the rate at which carbon monoxide is formed. If these rates are the same, then carbon monoxide must be formed by the oxidation or decomposition of formaldehyde. Let us denote the rate of formation of formaldehyde by w_{CH_2O} and the rate of its consumption by $k[CH_2O]$, then the rate of accumulation of formaldehyde $\frac{d[CH_2O]}{dt}$ can be written:

$$\frac{d\,[CH_2O]}{dt} = w_{CH_2O} - k\,[CH_2O].$$

so that the rate of consumption of formaldehyde is:

$$k\,[CH_2O] = w_{CH_2O} - \frac{d\,[CH_2O]}{dt}. \qquad (1)$$

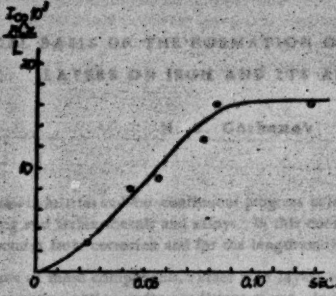


Fig. 2. Dependence of the activity of carbon monoxide on the time spent by the methane-air mixture in the reaction zone.

TABLE 2

Dependence of the Rates of Consumption of Formaldehyde and of Formation of Carbon Monoxide on the Time t spent by the Methane-Air Mixture in the Reaction Zone

t (seconds	Rate of consumption of formaldehyde k [CH_2O]	Rate of formation of carbon monoxide w_{CO} (mmoles/liter · second)	
		according to Equation 2	calculated by graphical differentiation of the kinetic formation curves.
0.024	1.2	1.5	2.0
0.043	4.4	4.0	4.3
0.056	7.3	8.6	6.2
0.077	11.2	12.9	11.8
0.083	10.6	12.9	12.9

SUMMARY

1. A study was made of the kinetics of the oxidation of methane in presence of formaldehyde labeled with radioactive carbon.

2. It was shown by a kinetic method that, in the oxidation of methane, carbon monoxide is formed mainly from formaldehyde.

Received May 18, 1955

Institute of Chemical Physics of the USSR
Academy of Sciences

LITERATURE CITED

[1] A. B. Nalbandyan, Proc. Acad. Sci. USSR, 60, 607 (1948); J. Phys. Chem. 22, 1443 (1948).

[2] M. B. Neiman, J. Phys. Chem. 28, 1235 (1954).

[3] G. I. Feklisov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, No. 4, 587 (T.p. 527)*.

* T. P. = C. B. Translation pagination

PHYSICOCHEMICAL BASIS OF THE FORMATION OF DIFFUSIONAL SURFACE LAYERS ON IRON AND ITS ALLOYS

N. S. Gorbunov

The development of new industries and the continuous progress being made in technology demand the application of new, extremely strong and stable metals and alloys. In this connection the need arises for the protection of metal components and structures from corrosion and for the lengthening of their useful lives.

It is the external surface of these components, rather than layers below the surface, that is subjected to the most severe mechanical and corrosive action under conditions of use. In industry, therefore, methods of protecting the surface layer by hard-wearing and corrosion-resistant coverings – formed either by electrolysis or by diffusion – are widely adopted. When the diffusing elements are nitrogen or carbon, only the diffusion method of application is possible, since these elements do not form ions in solution. Diffusion methods, however, are used also for the surface application of metals that can be applied also by electrolysis.

Diffusional surface treatment with metals has an important advantage over electrolytic deposition, namely, that the bonding of the applied metal to the base metal is much stronger, owing to the formation of a diffusional intermediate layer between the base metal and the surface. Moreover, the gradual fall in the concentration of the metal through the depth of the diffusion layer is associated with a more gradual change in properties in the transition from the base metal to the surface.

By the application of different elements, it is possible to vary the properties of the surface layer of the treated metal within wide limits. For example, by the application of zinc or aluminum, the properties of the surface layers are improved with respect to the action of certain corrosive agents, whereas saturation of the surface with carbon results only in an improvement in mechanical properties. When, however, the surface of iron is saturated with nitrogen, chromium, silicon, or certain other elements, the surface layers are improved both with respect to mechanical properties, and also with respect to stability against the action of corrosive agents.

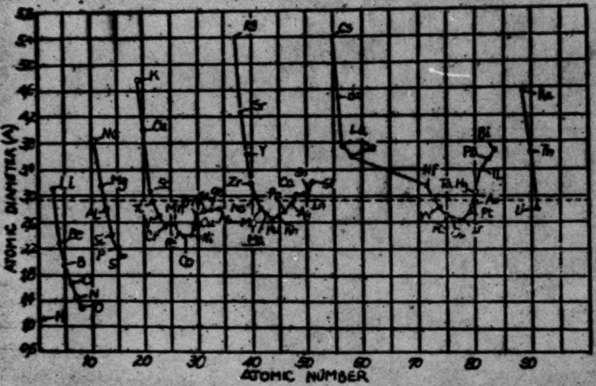
In diffusional treatments, either chemical compounds, or solid solutions, or both simultaneously may be formed in the surface layer of the metal. When a chemical compound is formed, the atoms of the applied element and of the metal-solvent combine together in definite proportions, and the solid phase consisting of this chemical compound can be denoted by a definite chemical formula. More frequently, however, the formation of continuous or limited solid solutions is observed in diffusional surface layers.

The work of Nikitin [1], Ageev [2], Kornilov [3], Grimm [4], Hume-Rothery [5], Kuznetsov [6], and other authors has indicated that the most important conditions affecting the formation of solid solutions are the dimensions and types of the crystalline lattices of the interdiffusing substances, and also the difference in atomic diameter. These same conditions apply also to the formation of diffusional surface layers.

Izgaryshev and Parfenova [7] established the existence of a definite relationship between the process of diffusional surface treatment and the conditions for the formation of chemical compounds and solid solutions between the metal to be treated and the substance applied.

However, in most papers on the process of diffusional metallization and the properties of the diffusional surface layers formed, no soundly based conclusions are stated regarding the possibility of the surface application of various substances to iron and its alloys. In the present investigation we sought to establish a relationship between the process of forming diffusional surface layers on iron and its alloys and the positions of the applied elements in Mendeleev's periodic system.

As already indicated, one of the main factors determining the possibility of forming solid solutions and diffusional surface layers is the difference between iron and the substance applied in atomic diameter. When the atomic diameter of the element diffusing into the metal to be covered is less than that of iron, or is greater, but not by more than 14-15%, distortion will occur in the crystal lattice of iron to an extent that will increase as the difference in atomic diameter increases. When the diffusing atoms are 14-15% greater in diameter than those of the base metal, the crystal lattice of the metal-solvent will be deformed to its limit, and this difference in atomic diameters will therefore be a critical limit. In the diffusion of elements whose atomic diameters are more than 15% greater than the atomic diameter of the metal-solvent, the distortion in the crystal lattice of the latter will be so great that surface breakdown will occur. Hence, the relative values of the atomic diameters of the interacting elements evidently determine the possibility of forming solid solutions and of diffusional surface layers on the metal.



When we arrange the elements according to their atomic diameters and atomic numbers [8], we can establish the zone for solubility in iron and mark the boundary that will enable us to determine which elements can form diffusional surface layers on iron and its alloys. The atomic diameter of α-iron is 2.54 A, so that the upper limit of atomic diameter for elements capable of diffusing into iron will be 2.94 A.

In the figure we give data on the dependence of the atomic diameters of the elements on their atomic numbers. The upper limit of atomic diameter for elements that can form diffusional surface layers is indicated by a broken line. It must be assumed that elements below this line can give diffusional surface layers, but those that are above it cannot.

Apart from these dimensional relationships, for the formation of a diffusional surface layer it is essential also that the element applied should have a definite solubility in iron. Hence, the main factors determining the possibility of the formation of diffusional surface layers are 1) the type and parameters of the crystal lattices, 2) the values of the atomic diameters, 3) definite solubility of the applied element in iron.

EXPERIMENTAL

Our investigation of the formation of diffusional surface layers on iron and its alloys fully confirmed the existence of these fundamental physicochemical conditions for the formation of such diffusional layers. Results from the literature [8,9] and our own experimental results on the formation of surface layers on iron and its alloys are given below in tables. In the next to the last column, the value of the solubility of the element in iron (% by weight) is accompanied by an indication in parentheses of the temperature at which the solubility was determined. In the last column of the table it is stated whether or not the given element forms a diffusional surface layer.

The diffusional surface treatment, except in the cases indicated by an asterisk, was carried out in the Dispersed System Section of the Institute of Physical Chemistry of the USSR Academy of Sciences, which is under the directorship of P. A. Rebinder. The diffusional treatment of surfaces of iron and iron alloys was carried out by various methods, and the processes were performed in various atmospheres: a hydrogen reducing atmosphere, a mixture of hydrogen and hydrogen chloride, an atmosphere of gaseous chlorine, and also a vacuum in the case of a new method of diffusional metallization that we have developed. The starting materials for the application of the coverings were pure metal powders, or, in rare cases, alloys of the metals with iron.

In the tables the results on the diffusional surface treatment of iron and its alloys are arranged according to the groups and subgroups in Mendeleev's periodic system.

The data in Table 1 show that elements of Subgroup A do not form diffusional surface layers. Of the elements of Subgroup B, copper and gold form such layers, but silver does not on account of its lack of solubility in iron.

Of the metals of Group II, only beryllium and zinc give diffusional surface layers, whereas the remaining metals do not, since they are insoluble in iron and the difference in atomic diameter exceeds 15%.

TABLE 1

Diffusional Surface Layers Formed by Elements of Group I of the Periodic System

Element	Atomic diameter (A)	Difference in atomic diameter (%)	Solubility of element in iron at		Diffusional surface layer
			room temperature	high temperature	
Subgroup A					
Lithium	3.13	23	0	0	Not formed
Sodium	3.83	50	0	0	"
Potassium	4.76	87	0	0	"
Rubidium	5.40	116	0	0	"
Cesium	5.40	116	0	0	"
Subgroup B					
Copper	2.55	1	0.35	8.0 (1094)	Formed
Silver	2.88	13	0	0	Not formed
Gold	2.87	13	0.6	15.0 (1170)	Formed

TABLE 2

Diffusional Surface Layers Formed by Elements of Group II of the Periodic System

Element	Atomic diameter (A)	Difference in atomic diameter (%)	Solubility of element in iron at		Diffusional surface layer
			room temperature	high temperature	
Subgroup A					
Beryllium*	2.25	− 11	4.5	6.0 (1150)	Formed [10]
Magnesium	3.20	25	0	0	Not formed
Calcium	3.93	55	0	0	"
Strontium	4.29	69	0	0	"
Barium	4.48	76	0	0	"
Subgroup B					
Zinc	2.74	9	6.0	Unknown	Formed
Cadmium	3.04	20	0	0	Not formed
Mercury	3.10	22	0	0	"

Of the elements of Group III, boron and aluminum form diffusional surface layers and thallium does not; there are no available data for the remaining elements of this group.

Of the elements of Group IV, titanium, carbon, and silicon form diffusional surface layers and lead does not; there are no data for the remaining elements.

Metals of Group V, Subgroup A, have cubic body-centered crystal lattices, like iron, and they do not differ from iron by more than 15% in atomic diameter. Moreover, they are fairly soluble in iron, particularly at high

TABLE 3

Diffusional Surface Layers Formed by Elements of Group III of the Periodic System

Element	Atomic diameter (A)	Difference in atomic diameter (%)	Solubility of element in iron at room temperature	Solubility of element in iron at high temperature	Diffusional surface layer
		Subgroup A			
Boron	1.94	−24	0.06	0.15 (1174)	Formed
Aluminium	2.80	10	32.0	35.0 (1232)	"
Scandium	3.02	19	Unknown	Unknown	–
Yttrium	3.62	40	"	"	–
		Subgroup B			
Gallium	2.74	9	Unknown	Unknown	–
Indium	2.13	−23	"	"	–
Thallium	3.43	35	0	0	Not formed

TABLE 4

Diffusional Surface Layers Formed by Elements of Group IV of the Periodic System

Element	Atomic diameter (A)	Difference in atomic diameter (%)	Solubility of element in iron at room temperature	Solubility of element in iron at high temperature	Diffusional surface layer
		Subgroup A			
Titanium	2.93	15	3.0	6.0 (1295)	Formed
Zirconium	3.19	25	0.15	Unknown	–
Hafnium	3.17	25	Unknown	"	–
		Subgroup B			
Carbon	1.54	−40	0.02	1.7 (1145)	Formed
Silicon	2.34	−8	15.0	18.5 (1195)	"
Germanium	2.78	10	Unknown	Unknown	"
Tin	3.16	23	8.0	16.0 (1110)	–
Lead	3.49	37	0	0	Not formed

TABLE 5

Diffusional Surface Layers Formed by Elements of Group V of the Periodic System

Element	Atomic diameter (A)	Difference in atomic diameter (%)	Solubility of element in iron at room temperature	Solubility of element in iron at high temperature	Diffusional surface layer
		Subgroup A			
Vanadium	2.69	6	100	100	Formed
Niobium	2.94	15	0.5	12.0 (1350)	"
Tantalum	2.94	15	0.17	6.5	"
		Subgroup B			
Nitrogen •	1.42	−44	0.015	Unknown	Formed [11]
Phosphorus	2.20	−13	1.0	2.8 (1050)	–
Arsenic	2.80	10	5.0	7.0 (830)	Formed
Antimony	3.23	27	7.0	8.0 (998)	Not formed
Bismuth	3.64	43	0	0	"

TABLE 6

Diffusional Surface Layers Formed by Elements of Group VI of the Periodic System

Element	Atomic diameter (A)	Difference in atomic diameter (%)	Solubility of element in iron at		Diffusional surface Layer
			room temperature	high temperature	
Subgroup A					
Chromium	2.57	1.5	100	100	Formed
Molybdenum	2.80	10	5.0	34.0 (1440)	"
Tungsten	2.82	11	8.0	33.0 (1525)	"

TABLE 7

Diffusional Surface Layers Formed by Elements of Group VII of the Periodic System

Element	Atomic diameter (A)	Difference in atomic diameter (%)	Solubility of element in iron at		Diffusional surface layer
			room temperature	high temperature	
Subgroup A					
Manganese	2.60	2	100	100	Formed
Technetium	—	—	—	—	—
Rhenium	2.75	8.2	29.0	Unknown	—

temperatures. Consequently, they all form diffusional surface layers. Of the elements of Group V, Subgroup B, nitrogen and arsenic form diffusional surface layers, but antimony and bismuth do not. Of the elements of Groups VI and VII, the metals of the A subgroups are of interest.

All metals of Group VI, Subgroup A, form diffusional surface layers, the data for these metals being similar to those for metals of Group V, Subgroup A.

Of the metals of Group VII, Subgroup A, manganese forms diffusional surface layers, but there are no data for technetium and rhenium.

Hence, an examination of the process of the formation of diffusional surface layers on iron and its alloys by the elements, as arranged in the groups and subgroups of Mendeleev's system, leads to the conclusion that the tendency for this process to occur depends on the structures and parameters of the crystal lattices of iron and of the applied element, on the difference in atomic diameter between iron and the applied element, and on the solubility of the applied element in iron in the solid state at ordinary and elevated temperatures. We consider that these conclusions regarding the diffusional surface treatment of iron and its alloys can be applied also to the similar treatment of other metals and complex alloys.

In conclusion the author wishes to express his great indebtedness to Dr. V. I. Likhtman for valuable discussions.

SUMMARY

1. The principal physicochemical conditions for the formation of diffusional surface layers on iron and its alloys are stated.

2. Diffusional layers are formed at the surface of the base metal as a result of the penetration of the applied substance into the crystal lattice of the metal-solvent.

3. The main physicochemical conditions determining the possibility of the formation of diffusional surface layers are: similarity in type between the crystal lattices of the applied element and of iron, a diffusing element of smaller atomic diameter than iron (if it is greater, then the difference in atomic diameter must not be more than 15%), and, finally, adequate solubility of the applied element in iron at ordinary and elevated temperatures.

4. These fundamental physicochemical conditions for the formation of diffusional surface layers are quite general and can be applied to the diffusional surface treatment of other metals and alloys.

Received December 15, 1954.

Institute of Physical Chemistry
of the USSR Academy of Sciences

LITERATURE CITED

[1] B. A. Nikitin, Prog. Chem., 13, No. 6, 417 (1944).

[2] N. V. Ageev, Chemistry of Alloys, Acad. Sci. USSR Press, Moscow, 1941; N. V. Ageev, Bull. Sector Phys. Chem. Anal., 8, 175 (1938); Nature of the Chemical Bond in Alloys, Acad. Sci. USSR Press, Moscow 1947.

[3] I. I. Kornilov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1945, No. 2, 104; 1947, No. 4, 337; 1948, No. 4, 370; 1949, No. 5, 449.

[4] H. G. Grimm, Handb. d. Phys. 24, No. 5, 466 (1927).

[5] W. Hume-Rothery, Structure of Metals and Alloys, State United Sci. Tech. Press, Moscow, 1938.

[6] V. G. Kuznetsov, Bull. Sector Phys. Chem. Anal., 16, No. 4, 69 (1948).

[7] M. I. Parfenova and N. A. Izgaryshev, J. Appl. Chem., 25, 7, 752(1952) (T. P. 831)*.

[8] I. I. Kornilov, Iron Alloys, Vol. 2, Acad. Sci. USSR Press, Moscow, 1951.

[9] M. Hansen, Structure of Binary Alloys, Vol. 1 and 2, Metallurgy Press, Moscow, 1941.

[10] E. I. Kontorovich, Bull, Metal Indust., No. 12 (1939).

[11] S. F. Yuryev, Nitridation of Steel and its Application in the Construction of Automobiles and Tractors, United Sci. Tech. Press, 1938; I. E. Kontorovich, Nitridation of Steel and the Properties of the Nitrided Layer, United Sci. Tech. Press, Moscow, 1938; Yu. M. Lakhtin; Physical Basis of the Nitridation Process, State Machinery Press, 1948.

---

*T. p. = C. B. Translation pagination.

DETERMINATION OF THE CRYSTALLIZATION COEFFICIENT FOR THE DISTRIBUTION OF A THORIUM B (RADIOACTIVE LEAD) SALT BETWEEN A SALT MELT AND CRYSTALS OF AN ISOMORPHOUS SALT

V. R. Klokman, V. K. Zinovyeva, and I. A. Tseveleva

Experimental investigations [1], carried out by one of us in collaboration with Khlopin, on the distribution of a micro component between a melt and a solid phase isomorphous with the micro component were confined to the distribution of radium between a melt and the crystals of a salt isomorphous with the corresponding radium salt. These investigations showed that in all of the systems studied the crystallization coefficient of radium for distribution between melt and an isomorphous salt at 300-600° was always less than its crystallization coefficient for distribution between a solution and the same isomorphous salt; the numerical value of the crystallization coefficient was never greater than unity. This indicates the absence of enrichment of the isomorphous solid phase with radium during crystallization from the melt.

Khlopin, Klokman, Murin, and Nefedov [2], in a study of the mechanism of the attainment of equilibrium with respect to the micro component during the separation of the solid phase from the melt, showed that, in the melt, as in the solution equilibrium distribution of radium occurred by a process of recrystallization. However, in the melt at relatively high temperatures the process is much more rapid. The equilibrium value of the crystallization coefficient of radium in the recrystallization of excess of barium nitrate in a melt of constant composition was attained in four hours at 315° and in one hour at 465°. The present investigation had the object of verifying these peculiarities in behavior for another micro component, namely, the radioactive isotope of lead ThB.

A study of the distribution of the radioactive isotope of lead RaD between solution and crystals of barium chloride and of barium nitrate at various temperatures was made by Polesitsky, who obtained the following values for the crystallization coefficients D: In the system $BaCl_2 - RaDCl_2 - H_2O$ $D_{100°} = 1.32$, and in the system $Ba(NO_3)_2 - RaD(NO_3)_2 - H_2O$ $D_{0°} = 0.16$ [3]. In the first case the solid phase was enriched in radioactive lead, even at 100°, and in the second case the liquid phase was enriched in micro component, even at 0°, and the crystallization coefficient was less than unity.

If the peculiarity that we have noticed — the non-enrichment of the isomorphous solid phase in micro component during crystallization from a melt — is a normal characteristic of the phenomenon, then for the distribution of ThB between melt and crystals of barium chloride the crystallization coefficient D should be less than or equal to unity, and for the distribution of ThB between melt and crystals of barium nitrate the crystallization coefficient D should be considerably less than unity. We were interested also in verifying, for another system, the time required for the establishment of equilibrium in the distribution of the micro component between the melt and crystals of an isomorphous salt. We determined the crystallization coefficients of ThB for the binary systems $Ba(NO_3)_2 - BaCl_2$ and $Ba(NO_3)_2 - NaNO_3$. The rate at which equilibrium with respect to the micro component was established was studied for the system $BaCl_2 - Ba(NO_3)_2$.

EXPERIMENTAL

Recrystallized, carefully dried barium chloride, barium nitrate, and sodium nitrate were used in the experiments. The temperature of the melts was measured with a thermocouple of platinum and platinum-rhodium, which was graduated without its pocket against the temperatures at which the crystallization of various salts begins. The experiments were carried out in porcelain crucibles. The melt was stirred with a quartz stirrer.

The radioactive isotope of lead ThB was prepared in the usual way by collecting the active deposit produced by thoron on a negatively charged platinum plate. The active deposit from thoron was then removed from the plate by boiling it for a few minutes in 0.1 N HNO_3 containing a small fraction of a milligram of lead nitrate. The active solution so obtained was evaporated in the crucible in which the experiment was to be performed. The inactive lead was added to reduce adsorption on the crucible walls and stirrer during the experiment.

The experimental procedure for the determination of the crystallization coefficient of ThB did not differ in principle from that which we used for similar determinations on radium [1]. The only difference was that, instead of the special pipets that we used previously for taking melt samples, in this work samples of the initial melt were taken with simple glass tubes (diameter 8 mm) and test samples of the final melt were taken with tubes whose end were drawn out to form capillaries. Two duplicate test samples were taken on each occasion.

The cooled samples of melt were extracted from the tubes and dissolved in hot 0.1 N HNO_3. Lead nitrate (5 mg) was added to each solution, and was then precipitated by hydrogen sulfide in weakly ammoniacal solution. On the next day the lead sulfide was filtered off onto a small piece of sensitive filter paper, which was laid on an aluminum dish having a perforated bottom. The dish was placed on a special test tube having a wide flat rim, which was previously greased so that the dish made close contact with the test tube. The test tube was provided with a side tube, which was attached to a water pump. The precipitates were dried in a drying cupboard at 60-70°, and their activities were then measured with a β-counter. The mean error of the activity measurements was ± 2%.

Determination of the Crystallization Coefficient for the Distribution of ThB between the Melt and Barium Chloride Crystals in the System $BaCl_2 - Ba(NO_3)_2$. According to the literature [4], the system $BaCl_2 - Ba(NO_3)_2$ is a simple binary system having a eutectic point at 497° and 37.3 mole % of barium chloride. On the fusion curve that we determined, the eutectic was found to be at 503° at a composition of 37.3 mole % of barium chloride, which is in quite satisfactory agreement with the reported data.

We determined the amount of ThB passing into the solid phase by measuring the activity of the melt before and after the separation of various amounts of barium chloride. The separation of solid phase from the saturated melt was carried out by the gradual lowering of the temperature of the original melt to the crystallization temperature of the previously selected final melt. The final melt was the same in all experiments (40 mole % of barium chloride, i.e. 8 g of $Ba(NO_3)_2$ and 4.285 g of $BaCl_2$; crystallization temperature 525°). The amount of solid phase separating was 0.4-1.4 g of $BaCl_2$, i.e. 2.9-11.5% of the total amount of barium ions in the melt (both ions derived from barium chloride and also ions derived from barium nitrate).

TABLE 1

Expt. No.	Amount separating into the solid phase		D
	Ba (%)	ThB (%)	
1	2.9	2.1	0.72
2	3.9	3.0	0.77
3	5.2	4.5	0.86
4	7.3	6.4	0.87
5	8.0	6.5	0.80
6	8.3	7.1	0.85
7	9.1	7.5	0.81
8	11.5	9.0	0.76
		Mean	0.80 ± 5%

The crystallization coefficient D was calculated from the formula:

$$D = \frac{x(100-y)}{y(100-x)},$$

in which x and y are the percentages of micro and macro component, respectively, passing into the solid phase, and (100−x) and (100−y) are the percentages of micro and macro component remaining in the melt. The results of the experiments on the determination of the crystallization coefficients for the distribution of ThB between the melt and barium chloride crystals are given in Table 1.

It will be from these results that the crystallization coefficient D remains constant within ± 5% for a 3.5-fold variation in the amount of solid phase separated. It was found, as expected, that the crystallization coefficient of ThB in this system is less than unity, so that in this case no enrichment of the solid phase in micro component occurs.

Determination of the Crystallization Coefficient for the Distribution of ThB between the Melt and Barium Nitrate Crystals in the Binary Systems $Ba(NO_3)_2$ and $Ba(NO_3)_2 - NaNO_3$ and $Ba(NO_3)_2 - BaCl_2$. The fusion curve that we determined for the binary system $Ba(NO_3)_2 - NaNO_3$ had a eutectic point at 296° and 11.6 mole % of $Ba(NO_3)_2$, which is in close agreement with the results of Harkins and Clark [5] [296° and 11.0 mole % of $Ba(NO_3)_2$] and with our own results [1] [297° and 11.1 mole % of $Ba(NO_3)_2$].

In the determination of the crystallization coefficient of ThB in this system we used two methods for the determination of the amount of ThB passing into the solid phase. On the one hand we determined the activity of the melt before and after the separation of the solid phase, and on the other hand we determined the activity of the solid phase itself. In the latter case, after the separation of the barium nitrate precipitate, the whole of the melt was drawn off as far as possible. The residue was washed from the crucible with 0.1 N HNO_3, and its activity was measured after precipitation as lead sulfide. The activity of interest to us — the activity of the $Ba(NO_3)_2$ precipitate — was determined as the difference between the activity of the whole residue and that of the remaining melt. In the calculation, the activity desorbed from the crucible walls during treatment of the residue with an acid solution was taken into account.

As we considered that in this system the crystallization coefficient D should be very small, the maximum possilbe amount of barium nitrate — about 60-75% — was separated into the solid phase. The absolute amount of barium nitrate which passed into the solid phase was about 5 g. The composition of the final melt was 16.8 mole % of $Ba(NO_3)_2$, and the temperature at which its crystallization began was 320°. The results of the experiments are given in Table 2.

TABLE 2

Expt. No.	Amount separating into the solid phase			D, calculated from the activity of the melt	D, calculated from the activity of the precipitate
	$Ba(NO_3)_2$ (%)	ThB			
		according to melt (%)	according to precipitate (%)		
1	60	4.7	8.2	0.03	0.06
2	75	16.0	16.0	0.06	0.06
3	75	4.0	11.1	0.01	0.04
4	75	9.9	5.6	0.04	0.02
5	75	22.8	21.3	0.09	0.09
			Mean	0.05 ± 0.02	0.05 ± 0.02

TABLE 3

Experiment No.	Time of crystallization	Amount of		D
		Ba separating into the solid phase (%)	ThB separating into the solid phase (%)	
1	15 minutes	8.8	1.0	0.10
2	30 minutes	9.1	4.9	0.51
3	45 minutes	9.2	5.6	0.59
4	1 hour	9.1	7.1	0.76
5	1 hour 15 minutes	9.2	7.9	0.85
6	1 hour 30 minutes	9.2	7.8	0.83

As can be seen from Table 2, our experimental results show that ThB is indeed not greatly entrained by the separating barium nitrate crystals. As regards the absolute value of the crystallization coefficient, we can say only that it is probably considerably less than unity, for, although the mean values of the crystallization coefficient obtained in two different ways are identical, the fluctuation in the values obtained in each series of experiments, even for the separation of a given amount of solid phase, are so great (about 50%) that we cannot say for certain whether or not we are dealing here solely with isomorphous cocrystallization. It is probable that in this system, which is made up entirely of nitrates, partial decomposition of lead nitrate occurs and is followed by adsorption of decomposition products on the surface of barium nitrate crystals. In order to verify this hypothesis, we determined the crystallization coefficient for the distribution of ThB between the melt and barium nitrate crystals in another system — $Ba(NO_3)_2$ — $BaCl_2$ — in which we had already determined the crystallization coefficient for the distribution of ThB between the melt and barium chloride crystals, and obtained agreeing results.

Three experiments were carried out on this system. In these experiments, 33%, 52%, and 67% of the total amount of barium ions were separated as solid phase. The experiments were carried out at 520°. In all cases, even when 67% of the barium ions was separated into the solid phase, no entrainment of ThB by the crystals could be detected. These results confirm our supposition that in the crystallization of the solid phase from the melt, either there will be no isomorphous coprecipitation at all of ThB with barium nitrate crystals, or the crystallization coefficient of ThB will be so small in this case, that, with the accuracy with which we can measure the activities of the initial and final melts, we shall not be able to detect the entrainment of ThB by the solid phase. Moreover, these results indicate also that no decomposition of lead nitrate occurs in the system $Ba(NO_3)_2$—$BaCl_2$ in spite of the higher temperature of the experiment.

Determination of the Rate of Attainment of Equilibrium for the Distribution of ThB between Melt and Crystals of Barium Chloride. In order to determine the rate of attainment of equilibrium with respect to the micro component in the distribution of ThB between melt and crystals of barium chloride, we carried out the recrystallization of a given amount (0.8 g) of barium chloride (finely ground and passed through a cambric sieve) in a melt of constant composition (40 mole % of $BaCl_2$) at constant temperature (525°) for various intervals of time. The time of recrystallization was varied from 15 to 90 minutes. The amount of ThB passing into the solid phase was determined from the difference in the activity of the melt, before and after the recrystallization of the solid phase in it. The results of the experiments are given in Table 3.

As can be seen from Table 3, as the time of recrystallization was increased, the value of the crystallization coefficient approached more and more closely to its equilibrium value, and, within the limits of experimental error, the equilibrium of D was attained already after one hour. These results are in accord with our previous results on the attainment of equilibrium in the distribution of radium between melt and crystals of barium nitrate [2]. In this case also, the equilibrium value of the crystallization coefficient of radium was attained in one hour at 465°.

In conclusion, we wish to thank Prof. A. P. Ratner for valuable discussions.

SUMMARY

1. The crystallization coefficient for the distribution of ThB between a salt melt and barium chloride crystals was determined (D = 0.80).

2. It was shown that the crystallization coefficient for the distribution of ThB between a salt melt and barium nitrate crystals is much less than unity.

3. It was established that in the distribution of the radioactive isotope of lead ThB between salt melts and crystals of isomorphous salts, no enrichment of the solid phase in the micro component occurs.

4. It was shown that, at about 500°, a state of equilibrium in the distribution of ThB between a melt and an isomorphous solid phase is established in one hour.

LITERATURE CITED

[1] V. G. Khlopin and V. R. Klokman, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1949, No. 3, 254; V. G. Khlopin, V. R. Klokman, and E. G. Pekelnaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, No. 2, 250(T.p. 227)*.

[2] V. G. Khlopin, V. R. Klokman, A. N. Murin, and V. D. Nefedov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1950. No. 2, 127.

[3] A. E. Polesitsky, Trans. State Radium Inst., 2, 73 (1933).

[4] Technical Encyclopedia. Tables of Physical, Chemical, and Technological Constants, Vol. 7, 1931, p. 193.

[5] W. D. Harkins, G. L. Clark, J. Am. Chem. Soc., 37, 1816 (1915).

Received March 25, 1955

V. G. Khlopin Radium Institute
of the USSR Academy of Sciences

---

* T. p. = C. B. Translation pagination.

ROLE OF DISSOCIATIONAL ACTIVATION IN THE SINTERING OF OXIDES OF ELEMENTS OF VARIABLE VALENCY

A. I. Leonov

It is known that the sintering occurring during the firing of ceramics and refractories is affected by the surrounding atmosphere of gases. The effect of the atmosphere is most marked for oxides of elements of variable valency. In order to determine the mechanism by which the atmosphere affects the sintering of oxides, we have carried out expriments on the sintering of copper, iron, and magnese oxides.

EXPERIMENTAL

Copper carbonate, manganese carbonate, and iron oxalate were converted into the corresponding oxides by calcination at 600° for one hour. The oxides were compressed into rectangular bars 30 x 7 x 3 mm, under a pressure of 500 kg/sq.cm. The length of the sample was measured before and after the experiment, and the linear shrinkage was calculated. The samples were heated in a hermetically closed tube furnace. Evacuation was carried out by means of a rotary pump. Some of the experiments were carried out in argon.

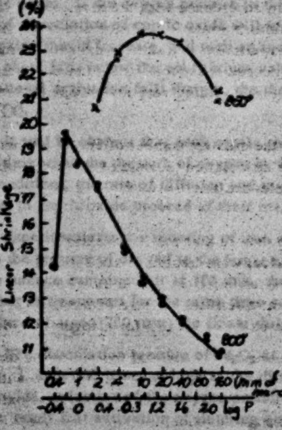


Fig. 1. Effect of oxygen pressure on the linear shrinkage of cupric oxide during firing. Duration of treatment at temperatures indicated, one hour

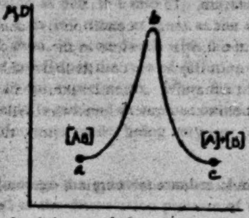


Fig. 2. Scheme of dissociational activation.

The sintering of cupric oxide was carried out at 800° and at 850°, the time of treatment being one hour. The results are shown in Fig. 1, in which the oxygen pressure (log p) at which the firing is carried out is plotted as abscissa. The oxygen pressure was taken to be 0.21 times the pressure of the air. The ordinates are values of the percentage linear shrinkage of the samples after a one-hour treatment.

As can be seen from Fig. 1, the linear shrinkage of a cupric oxide sample depends on the pressure of oxygen in the furnace. When sintering is carried out at 800°, diminution in the pressure of oxygen in the furnace is accompanied by increased linear shrinkage, which attains a maximum at about 0.5-1 mm of mercury; with further reduction in oxygen pressure, the shrinkage diminishes sharply. At 850° maximum sintering occurs at 10-20 mm of mercury. According to the literature [1], the dissociation pressure of cupric oxide ($2CuO \rightleftharpoons Cu_2O + 0.5O_2$) is about 1 mm at 800° and 10-15 mm at 850°. It will be seen that maximum shrinkage occurs when the oxygen pressure in the gas phase is equal to the dissociation pressure of cupric oxide. The shrinkage decreases both at higher and at lower oxygen pressures in the furnace.

We explain the observed effect of oxygen pressure on the sintering of cupric oxide by the occurence of dissociational activation. The concept of dissociational activation is based on the view that in the dissociation and association of a substance the molecules pass through an activated transition state. In this transition state the molecules have a higher rate of diffusion and higher chemical activity than molecules in the stable state. Such a process is represented diagrammatically in Fig. 2, in which D is the coefficient of diffusion, μ is the chemical activity, [AB], [A], and [B] represent stable states of the molecules, and the curve $\underline{abc}$ represents the variation of the coefficient of diffusion and chemical activity of molecules in the transition state.

The greater the number of reversible changes (dissociation $\rightleftharpoons$ association) undergone by each molecule of a substance in unit time, the more vigorously will chemical and physical processes take place in this substance (chemical reactions, crystallization, sintering). The kinetics of such processes, therefore, depend on the degree of dissociation of the substance, which can be calculated from the free energy of formation of the compound, or determined by measuring the dissociation pressure of the oxide. The degree of dissociation of an oxide can be varied by change in temperature or by change in the pressure of oxygen in the gas phase.

The effect of oxygen pressure on the degree of dissociation of cupric oxide can be ascertained with the aid of the mass-action law, which for the dissociation reaction AB $\rightleftharpoons$ A + B can be expressed by the equation:

$$\frac{[A][B]}{[AB]} = K,$$

in which [AB] is the concentration of the substance AB, [A] and [B] are the concentrations of the dissociation products, and K is the equilibrium constant.

If we increase the concentration of, for example, B by adding an extra amount of this to the system then since K is a constant, [A] will diminish and [AB] will increase, i. e. addition of one of the dissociation products will lower the degree of dissociation. The dissociation pressure of cupric oxide at 800° is 1 mm [1], and the partial pressure of oxygen in the air under normal conditions is about 160 mm, i. e. is 160 times as great as the dissociation pressure of cupric oxide. If the oxygen pressure in the furnace is lowered, then, in accordance with the mass-action law, the degree of dissociation of cupric oxide will increase. Under these conditions the rate of diffusion and reactivity of cupric oxide should increase, and such an increase was observed in our experiments. When the oxygen pressure in the gas phase falls below the equilibrium value, all the cupric oxide is reduced to cuprous oxide and the extent of dissociational activation falls sharply, the dissociation pressure of cuprous oxide being very low (about 10^{-6} mm) at 800° [1].

It will be obvious that each cupric oxide molecule will undergo the greatest number of acts of dissociation in unit time when the pressure of oxygen in the gas phase is equal to the dissociation pressure of the oxide. Under these conditions, the rate of diffusion and the reactivity of oxide molecules are at a maximum, and all kinetic processes in cupric oxide proceed at their maximum rates.

Experiments on the sintering of iron and manganese oxides again showed that the linear shrinkage is dependent on the pressure of oxygen in the furnace. For example, when the oxides were treated at 1000° for one hour and the furnace contained air at 760 mm, the linear shrinkages were 20% for ferric oxide and 21.5% for manganic oxide, but in treatments for the same time and at the same temperature at a residual pressure of 2 mm or in an atmosphere of argon (760 mm) the linear shrinkages rose to 24% for ferric oxide and 24.8% for manganic oxide.

The dissociation pressure of Fe_2O_3 at 1000° is 0.3 mm [2], and the partial pressure of oxygen in the air is 160 mm, i. e. is 533 times as high as the dissociation pressure of Fe_2O_3. In these experiments, as in those with cupric oxide, reduction of the oxygen pressure in the furnace increases the degree of dissociation of ferric oxide, with the result that activation of sintering occurs. The same is true of manganic oxide.

Analogous results were obtained by Budnikov and Tresvyatsky [3] in a study of the effect of the gaseous medium on the tendency of chromic oxide to sinter. Their experiments showed the sintering of Cr_2O_3 is poor when it is fired in an oxidizing medium. If, however, the chromic oxide if fired in absence of oxygen — for example, in argon, in nitrogen, or in a vacuum — it sinters very readily, forming a compact crystalline material. The results of the experiments are given in the table.

On the basis of these experiments, Buknikov and Tresvyatsky suggested that the cause of the poor sintering of chromic oxide in an oxidizing medium is the partial surface oxidation of the oxide with formation of hexavalent chromium ions. When the firing is carried out in a neutral gaseous medium, oxidation of the chromic oxide does

TABLE

Effect of the Gaseous Medium on the Sintering of Pure Chromic Oxide during Firing

Firing conditions	Firing temperature (°C)		
	1400	1500	1600
	True porosity (%)		
Firing in an oxidizing medium in a flame furnace	49.36	48.96	39.83
Firing in a vacuum furnace at a residual pressure of 1-3 mm	46.38	13.61	11.46
Firing in a neutral gas (nitrogen)	45.89	16.61	10.50

not occur and its sintering proceeds normally. According to our views, the cause of the satisfactory sintering of chromic oxide in a vacuum or in nitrogen, as compared with an oxidizing medium, lies in the following facts. The calculated dissociation pressure of Cr_2O_3 [2] at 2000° is 3 mm, and at 3000° 760 mm. At 1400-1600° it will be in the region of 0.1-0.01 mm. Under a reduced pressure of 1-3 mm or in an inert gas the oxygen pressure will be about one-hundredth of its value in an oxidizing medium (160 mm), so that in a vacuum or in nitrogen the degree of dissociation of Cr_2O_3 is higher and the processes of diffusion and sintering of Cr_2O_3 proceed more rapidly.

It will be evident from the above considerations that dissociational activation plays an important part in the sintering of oxides of elements of variable valency (Fe_2O_3, Cr_2O_3, Mn_2O_3, TiO_2, SnO_2, CuO, CoO, etc.). The phenomenon of dissociational activation must be taken into account in the technology of the manufacture and in the use of refractories (chromomagnesite, chromites, etc.), and in the manufacture of special ceramics (ferrites, titanates, stannates).

SUMMARY

1. The effect of the pressure of oxygen in the gaseous medium on the sintering of oxides of elements of variable valency is demonstrated.

2. The theory of dissociational activation is expounded. It provides an explanation of the mechanism of the action of oxygen on the chemical and physical processes occurring in oxides during firing.

3. The importance of the effect of dissociational activation on the synthesis and use of materials prepared from oxides of elements of variable valency is pointed out.

Received January 21, 1955

Institute of Silicate Chemistry of the USSR
Academy of Sciences

LITERATURE CITED

[1] Ya. I. Gerasimov and A. N. Krestovnikov. Chemical Thermodynamics in the Metallurgy of Nonferrous Metals, Vol. 2, United Sci. Tech. Press, 1932, p. 54.

[2] J. W. Mellor, Inorganic and Theoretical Chemistry, 13, London, 1943, P. 794.

[3] P. P. Budnikov and S. G. Tresvyatsky, Proc. Acad. Sci. USSR, 95, No. 5, 1041 (1954).

BLANK
PAGE

REACTION OF ALKYL 2-CHLOROVINYL KETONES WITH ETHYL ACETOACETATE

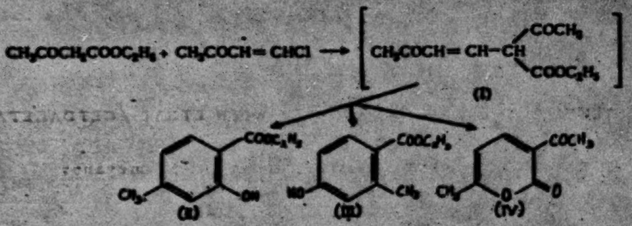
N. K. Kochetkov, L. I. Kudryashov, and A. N. Nesmeyanov

2-Chlorovinyl ketones are capable of undergoing a great variety of reactions, and various aliphatic, alicyclic, and heterocyclic compounds can be prepared by their aid [1]. However, the reaction of 2-chlorovinyl ketones with compounds containing an active methylene group, such as ethyl acetoacetate, has not been investigated. It is known that 3-(chloromethylene)camphor – which may be considered to belong, formally, to the class of 2-chlorovinyl ketones, although it differs considerably in chemical behavior from simple alkyl 2-chlorovinyl ketones – reacts with ethyl sodioacetoacetate in alcoholic solution with formation of ethyl $\Delta^{3,\beta}$-camphorpropionate [2]. This reaction is thus associated with simultaneous alcoholysis of an acetyl group. It was found that the same reaction carried out in an inert medium proceeds in a complex fashion, and no definite results were obtained [2]. Attempts have been made to effect the condensation of 2-chlorovinyl phenyl ketone with sodioacetoacetic and sodiomalonic esters in benzene, but again no positive results were obtained [3]

We have studied the reaction, under various conditions, of ethyl acetoacetate with 2-chlorovinyl methyl ketone. The reaction of ethyl sodioacetoacetate with 2-chlorovinyl methyl ketone in benzene did not give unequivocal results; the product obtained was a complex mixture formed as the result of obscure secondary reactions. Negative results were obtained also in the condensation of ethyl acetoacetate with 2-chlorovinyl methyl ketone in aqueous alkaline medium, in diethylaniline, and in presence of caustic potash in benzene. The use of acid condensing agents – zinc chloride and acetic anhydride – was also unsuccessful. A positive result was obtained in the reaction of 2-chlorovinyl methyl ketone only in presence of calcined potassium carbonate in benzene, toluene, or xylene. As yet, potassium carbonate is the only suitable condensing agent found. The reaction mixture, after the usual treatment, yielded ethyl 4-methylsalicylate. This was not the only substance formed in the condensation process, for a substance melting at 61° was also isolated, and preliminary investigation showed that this is a substance formed from the "bisketovinylated" • product and is probably a benzofuran derivative. The yield of substituted salicylic ester is increased by the use of excess of ethyl acetoacetate. Thus, when equimolecular amounts of reactants are used the yield is 10%, when a two-fold excess of ethyl acetoacetate is used the yield is 16%, for a five-fold excess it is 32%, and for a ten-fold excess it is 40%. The temperature also has some effect: in boiling benzene (five-fold excess of ethyl acetoacetate) the yield of the salicylic ester is 28%, in boiling toluene it is 32%, and in boiling xylene it is 34%. Higher-boiling solvents cannot be used because 2-chlorovinyl methyl ketone resinifies completely above 140-150°. The formation of a substituted salicylic ester as a result of this reaction can be represented as follows. 2-Chlorovinyl methyl ketone reacts with ethyl acetoacetate with formation of the normal "monoketovinylated" product (I) by reaction at the methylene group. We shall not consider the question of whether (I) is formed by direct ketovinylation at carbon, by migration of a ketovinyl group from oxygen in the original O-ketovinylated product, or by Michael condensation with subsequent dehydrohalogenation. This question requires special investigation, but it is obvious that initially an intermediate product of type (I) must be formed. The ketovinylation product (I) is able to undergo further reactions. It is particularly necessary to note that the hydrogen on the central carbon atom, being under the influence of three carbonyl groups, is highly mobile, so that the entry of a second ketovinyl group is greatly facilitated. The importance for the result of the reaction of an excess of ethyl acetoacetate now becomes understandable; this excess will naturally reduce the possibility of the second ketovinylation and the formation of reaction products of greater complexity. The cause of the lack of success in the condensation of a chlorovinyl ketone with ethyl sodioacetoacetate is also clear: the transmetallization of the monoketovinylation product by ethyl sodioacetoacetate will readily occur, and can be followed by a second substitution reaction.

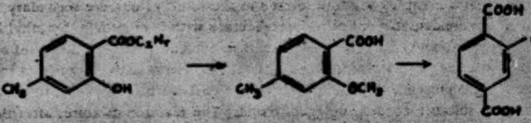
Under suitable reaction conditions the intermediate product (I) can also undergo cyclization; and in our case cyclization is, in fact, found to occur. It can occur in various ways, and of these we must consider three – formation of the 4-methylsalicylic ester (II), of its isomer (III), and of the 2H-pyran-2-one derivative (IV):

• We shall refer to the introduction of a ketovinyl group RCOCH=CH– into the molecule of an organic compound – which is usually effected by the action of a 2-chlorovinyl ketone – as "ketovinylation".

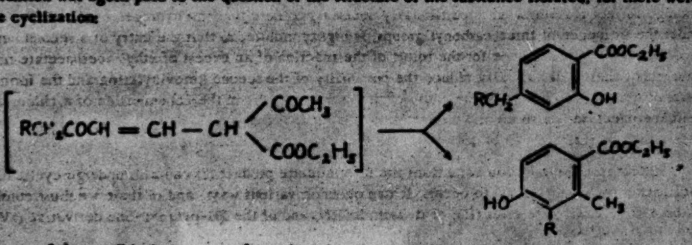


As regards the last compound (IV) we cannot assert that it is not formed in the reaction, since the by-products of the reaction included small amounts of substances whose structures were not established.

Our main attention, however, was given to the isolation of a hydroxytoluic ester, which was the main reaction product and was obtained, under optimum conditions, in yields of up to 40%. The choice between the two possible structures for this substance – (II) and (III) – was made on the basis of the following data. In aqueous solution the substance gave a color with ferric chloride, which is characteristic for salicylic acid derivatives; p-hydroxybenzoic acid derivatives do not give this reaction. Hydrolysis of the substance gave a crystalline acid that corresponded in properties to 4-methylsalicylic acid and could be decarboxylated to m-cresol. Final proof of the structure of the condensation product as a 4-methylsalicylic ester (II) was provided by its methylation with dimethyl sulfate followed by oxidation of the methylation product, which was not isolated in the pure form. The only reaction product obtained was methoxyterephthalic acid, the formation of which finally excludes the structure (III)

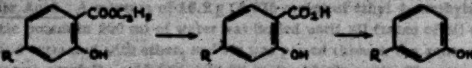


Hence, the cyclization of the ketovinylation product (I) proceeds in such a way that the carbonyl group of the ketovinyl residue reacts with the methyl of the acetyl group. Attempts were made to detect the presence of the second possible cyclization product (III), but we did not succeed in isolating this substance; it is evidently not formed in any appreciable amount. The reaction that we have discovered is of interest as a preparative method, inasmuch as all of the accepted methods for the preparation of 4-alkylsalicylic acids are based on the carbonation of m-alkylphenols [4, 5] or on related reactions [6-9]. However, the source of the required m-alkylphenols is coal tar, and no satisfactory synthetic methods of obtaining these, particularly the higher homologs, are known. We therefore attempted to extend our reaction to the preparation of the higher homologs of the 4-alkylsalicylic acids, and we obtained modest, but positive results. The higher alkyl 2-chlorovinyl ketones, namely, the ethyl, propyl, and isobutyl ketones, were found to react with ethyl acetoacetate under the same conditions in accordance with the same scheme, the corresponding 4-alkylsalicylic esters being formed; the yields of the latter, however, were low (about 20%). The reaction is evidently more complex, but in this case also the substituted salicylic ester was isolated without great difficulty. Special attention was again paid to the question of the structure of the substance isolated, for there were two possibilities in the cyclization:



It was found that only one of the possible isomers was formed, and attempts to detect the second isomer were not successful. The structures of the products were proved by experiments on the product of the condensation of 2-chlorovinyl propyl ketone with ethyl acetoacetate, which was taken as typical. Hydrolysis and decarboxylation gave a phenol having the properties of m-propylphenol, and methylation with dimethyl sulfate followed by oxidation gave methoxyterephthalic acid as sole product. This indicates that the course of the condensation reaction of higher alkyl 2-chlorovinyl ketones is the same as that of 2-chlorovinyl methyl ketone.

The 4-alkylsalicylic esters obtained are colorless oily liquids that can be preserved without change for a long time. The corresponding acids were prepared by hydrolysis with aqueous alkali; these are readily crystallizing solids (yields 60-90%). By decarboxylation of the acids, which proceeds smoothly by pyrolysis, high yields were obtained of the corresponding m-alkylphenols:



In view of the ready accessibility of the starting materials, the proposed method for the synthesis of inaccessible m-alkylphenols is undoubtedly of interest, in spite of the low yields obtained in the first stage of the synthesis.

EXPERIMENTAL

1. Ethyl 4-Methylsalicylate. A mixture of 260 g (2 moles) of ethyl acetoacetate, 30 g (0.22 mole) of finely ground potassium carbonate, and 100 ml of absolute toluene was prepared in a three-necked flask fitted with stirrer, dropping funnel, and reflux condenser and was boiled while being vigorously stirred. A solution of 21 g (0.2 mole) of 2-chlorovinyl methyl ketone in 100 ml of absolute toluene was added dropwise to the constantly heated mixture over a period of eight hours, and the mixture was then heated further for about one hour and left overnight. The precipitate was filtered off and washed carefully with benzene, and benzene and toluene were then distilled from the combined filtrates at 50-60 mm, and ethyl acetoacetate (about 100 g) was distilled off at 10 mm. The residue was vacuum-distilled, and a wide fraction boiling at 128-150° (10-30 mm) was collected; this was redistilled and yielded a fraction boiling at 128-132° (7 mm). Redistillation gave 14.2 g (39.2%) of ethyl 4-methylsalicylate, b.p. 129-132° (11 mm); d_4^{20} 1.0915; n_D^{20} 1.5174.

For ethyl 4-methylsalicylate the literature gives: b.p. 254° (760 mm)[10]; b.p. 133° (12 mm), d_4^{23} 1.0950 [11].

Found %: C 67.32; 67.26; H 7.04; 7.06

$C_{10}H_{12}O_3$. Calculated %: C 66.65; H 6.71

Ethyl 4-methylsalicylate is a colorless stable liquid. It gives a violet color with aqueous ferric chloride, and it forms a voluminous white precipitate of the phenoxide with aqueous caustic soda.

2. Ethyl 4-Ethylsalicylate. Reaction between 260 g (2 moles) of ethyl acetoacetate, 23.7 g (0.2 mole) of 2-chlorovinyl ethyl ketone, and 30 g of potassium carbonate in toluene was carried out as described above. When reaction was complete, 200 ml of water was added, and the toluene layer was separated and washed with two 100-ml portions of water. The aqueous extracts were extracted with three 100-ml portions of ether, and the ether extracts were combined with the toluene solution. The solution was dried over magnesium sulfate and distilled. The ether and toluene were distilled off at 30 mm, and the residue, distilled at 10 mm, yielded: Fraction I, b.p. up to 95°; Fraction II, b.p. 95-130°; and Fraction III, b.p. 130-152°. In a redistillation of Fraction II, distillate coming over below 112° (9 mm) was rejected, and the residue was combined with Fraction III. Two distillations of this combined fraction gave a substance of b.p. 129-133° (9 mm), which, when distilled once further, gave 5.8 g (18%) of ethyl 4-ethylsalicylate, b.p. 141-142° (15 mm); d_4^{20} 1.0784; n_D^{20} 1.5162. It is a stable colorless oily liquid, which gives a violet color with aqueous ferric chloride.

3. Ethyl 4-Propylsalicylate. Reaction between 286 g (2.2 moles) of ethyl acetoacetate, 29.5 g of 2-chlorovinyl propyl ketone, and 32 g (0.23 mole) of potassium carbonate in 250 ml of absolute xylene was carried out as described above. After treatment described for the preceding experiment, distillation yielded a fraction of b.p. 110-150° (6 mm). This was boiled with a sodium ethoxide solution (2 g of sodium in 50 ml of absolute alcohol) for two hours, and was then poured into 1500 ml of 2% sulfuric acid. The mixture was extracted with ether, and the extractewas dried over sodium sulfate. The ether was distilled off, and the residue was distilled under reduced presure, a fraction of b.p. 135-140° (6 mm) being collected. Redistillation yielded 7.7 g (17%) of ethyl 4-propylsalicylate, b.p. 138-140° (6 mm); d_4^{20} 1,0836 n_D^{20} 1.5165.

Found %: C 68.95; 69.14; H 7.70; 7.72

$C_{12}H_{16}O_3$. Calculated %: C 69.20; H 7.75

Ethyl 4-propylsalicylate is a colorless stable liquid. It gives a violet color with aqueous ferric chloride.

4. Ethyl 4-Isobutylsalicylate. Reaction between 164 g (1.26 moles) of ethyl acetoacetate, 18.5 g (0.12 mole) of 2-chlorovinyl isobutyl ketone, and 30 g (0.22 mole) of potassium carbonate in 150 ml of absolute xylene was carried out as described above. After the treatment described for the preparation of ethyl 4-ethylsalicylate, distillation gave a fraction of b.p. 145-152° (8 mm). Redistillation gave 4.9 g (18%) of ethyl 4-isobutylsalicylate, b.p. 148.5-150° (9 mm); d_4^{20} 1.0876; n_D^{20} 1.5118.

Ethyl 4-isobutylsalicylate is a colorless stable oil. It gives a violet color with alcoholic ferric chloride.

5. 4-Methylsalicylic Acid. A mixture of 13.2 g (0.075 mole) of ethyl 4-methylsalicylate with a solution of 8.4 g (0.15 mole) of caustic potash in 200 ml of water was boiled until all traces of oil disappeared (about two hours). The solution was cooled and extracted with ether, and air was passed through the aqueous layer to remove traces of ether. The aqueous layer was carefully acidified with 5% hydrochloric acid. The precipitate was filtered off, washed with cold water, and dried in a vacuum. Recrystallization from water gave 10 g (90%) of colorless needles, m.p. 175°. For 4-methylsalicylic acid the literature [12] gives m.p. 175°.

Found %: C 63.33; 63.31; H 5.49; 5.31

$C_8H_8O_3$. Calculated %: C 63.15; H 5.30

4-Methylsalicylic acid is readily soluble in alcohol and in ether; it is moderately soluble in hot water, and only slightly soluble in cold water. It gives a violet color with an aqueous solution of ferric chloride.

6. 4-Ethylsalicylic Acid. This acid was prepared in a similar way by the hydrolysis of 1.94 g of ethyl 4-ethylsalicylate. Recrystallization from water gave 1.16 g (70%) of colorless needles, m.p. 124°. For 4-ethylsalicylic acid the literature [6] gives m.p. 124°.

4-Ethylsalicylic acid is readily soluble in alcohol and in ether; it is very difficultly soluble in cold water, more readily in hot water. It gives a violet color with an aqueous solution of ferric chloride.

7. 4-Propylsalicylic Acid. This acid was prepared in a similar way by the hydrolysis of 8.0 g of ethyl 4-propylsalicylate. Recrystallization from water gave 5.8 g (90%) of colorless needles, m.p. 113°.

Found %: C 66.76; 66.67; H 6.94; 7.02

$C_{10}H_{12}O_3$. Calculated %: C 66.65; H 6.71

4-Propylsalicylic acid is readily soluble in alcohol and in ether, and is sparingly soluble in hot water. It gives a violet color with an aqueous solution of ferric chloride.

8. 4-Isobutylsalicylic Acid. This acid was prepared in a similar way by the hydrolysis of 2.8 g of ethyl 4-isobutylsalicylate. Recrystallization from a large volume of water yielded 1.5 g (62%) of colorless crystals, m.p. 87°.

Found %: C 68.12; H 7.47

$C_{11}H_{14}O_3$. Calculated %: C 68.02; H 7.27

4-Isobutylsalicylic acid is readily soluble in alcohol and in ether; it is insoluble in cold water, and is sparingly soluble in hot water. It gives a violet color with aqueous ferric chloride.

9. m-Cresol. A small distillation flask containing 3.8 g (0.025 mole) of 4-methylsalicylic acid was heated in a metal bath. At 275° the molten substance began to froth, and as decarboxylation occurred, so m-cresol distilled over. Redistillation gave 1.7 g (63%) of m-cresol, b.p. 201-202°; d_4^{20} 1.0253; n_D^{20} 1.5317; found MR 32.66; calculated for $C_7H_8OF_3$; MR 32.45. The literature [13, 14] gives for m-cresol: b.p. 201°, d_4^{20} 1.034; d_4^{18} 1.0363; n_D^{18} 1.5424.

Its benzoic ester was prepared in the usual way: glistening scales, m.p. 54° (from aqueous alcohol). The literature [15] give 54°.

10. m-Ethylphenol. This was prepared similarly from 2.6 g of 4-ethylsalicylic acid. Redistillation gave 1.4 g (70%) of m-ethylphenol, b.p. 217-218°; d_4^{20} 1.0218; n_D^{20} 1.5296; found MR 36.91; calculated for $C_8H_{10}OF_3$ MR 37.07. The literature [16, 17] gives for m-ethylphenol: b. p. 217°; d_4^{15} 1.0230; n_D^{16} 1.5340.

Its 3,5-dinitrobenzoic ester was prepared in the usual way by heating the substance with 3,5-dinitrobenzoyl chloride in pyridine. Recrystallization from alcohol gave light-yellow plates, m. p. 107°.

Found %: N 9.00; 9.08

Calculated %: N 8.86

11. m-Propylphenol. This was prepared similarly from 5.8 g of 4-propylsalicylic acid. Redistillation gave 3.6 g (80%) of m-propylphenol, b.p. 229-231°; d_4^{20} 0.9877; n_D^{20} 1.5223; found MR 42.07; calculated for $C_9H_{12}OF_3$, MR 41.69. The literature [18] gives for m-propylphenol: b.p. 117-118° (12 mm).

Found %: C 79.15; 79.20; H 8.82; 8.95

Calculated %: C 79.36; H 8.88

Its 3,5-dinitrobenzoic ester was prepared in the usual way. Recrystallization from aqueous alcohol gave light-yellow plates, m.p. 75°. For m-propylphenyl 3,5-dinitrobenzoate the literature [19] gives m.p. 77°.

12. Methylation and Oxidation of 4-Methylsalicylic Acid. A mixture of 7.6 g (0.05 mole) of 4-methylsalicylic acid and 12 ml (0.13 mole) of dimethyl sulfate was shaken for 30 minutes with a solution of 2.5 g of caustic soda in 30 ml of water. The mixture was heated to the boil, a further 4 g of caustic soda was added, and boiling was continued for four hours. The cooled mixture was acidified, and the precipitate was filtered off, washed with water, dissolved in a small amount of 3% potassium carbonate solution, and, in order to remove any original 4-methylsalicylic acid, treated with small amounts of potassium permanganate until there was a permanent coloration. The filtered solution was acidified, and the crystals of 4-methyl-o-anisic acid that separated were filtered off and subjected to oxidation without further purification. The oxidation was carried out by heating 0.08 g of the substance with excess of potassium permanganate in 30 ml of water at the boil for eight hours. The excess of permanganate was destroyed by the addition of alcohol, and the mixture was filtered. The filtrate was acidified and extracted with ether. The ether extract was extracted with 25 ml of 3% caustic soda. Air was blown through the alkaline solution to remove ether. The solution was then acidified, and the crystals of methoxyterephthalic acid that separated were filtered off. Recrystallization from water yielded colorless crystals, m.p. 280°. For methoxyterephthalic acid the literature [20] gives m.p. 281°.

13. 4-Propyl-o-anisic Acid. A mixture of 1.04 g (0.006 mole) of 4-propylsalicylic acid and 4 ml (0.006 mole) of dimethyl sulfate was shaken for 45 minutes with a solution of 0.5 g of caustic soda in 20 ml of water. The mixture was heated to the boil, 30 ml of 10% caustic soda was added, and boiling was continued for six hours. After the treatment described for the preceding experiment a crystalline precipitate was obtained. Recrystallization from aqueous alcohol gave colorless crystals, m.p. 80.5°.

Found %: C 67.89; 67.73; H 7.16; 7.13

$C_{11}H_{14}O_3$. Calculated %: C 68.02 H 7.27

4-Propyl-o-anisic acid is readily soluble in alcohol and in ether, but is almost insoluble in water. It does not give a color with ferric chloride solution.

14. Oxidation of 4-Propyl-o-anisic Acid. The oxidation of the acid (0.64 g) was carried out as described for Experiment 12. Recrystallization from water gave methoxyterephthalic acid, m.p. 291°. In admixture with the substance obtained in Experiment 12 there was no depression in melting point.

SUMMARY

1. By the condensation of alkyl 2-chlorovinyl ketones with ethyl acetoacetate in presence of potassium carbonate in an inert solvent, the corresponding 4-alkylsalicylic esters were obtained. The possible mechanism of the reaction is examined.

2. The structure of the resulting compounds was proved by methylating the methyl and propyl homologs and then oxidizing the products to methoxyterephthalic acid.

3. The 4-alkylsalicylic esters were hydrolyzed with aqueous alkali to the corresponding acids, and these were then decarboxylated with formation of the corresponding m-alkylphenols in good yield.

LITERATURE CITED

[1] A. N. Nesmeyanov, N. K. Kochetkov, and M. I. Rybinskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 4, 350; 1951, No. 3, 395; 1953, No. 3, 479 (T.p. 429)*; Proc. Acad. Sci. USSR 93, 72 (1953); N. K. Kochetkov,

---

* T. p. = C. B. Translation pagination.

Proc. Acad. Sci. USSR 84, 289 (1952); 82, 593 (1952); Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, No. 6, 991 (T.p. 883)*; A. N. Nesmeyanov and N. K. Kochetkov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1951, No. 6, 686; A. N. Nesmeyanov, N. K. Kochetkov, and L. A. Matov, Proc. Acad. Sci. USSR, 92, 85 (1953); A. N. Nesmeyanov, N. K. Kochetkov, M. Ya. Karpeisky, and G. V. Aleksandrova, Proc. Acad. Sci. USSR, 92, 409 (1952); N. K. Kochetkov, M. I. Rybinskaya, and A. N. Nesmeyanov, Proc. Acad. Sci. USSR, 79, 799 (1951); N. K. Kochetkov and G. V. Aleksandrova, Proc. Acad. Sci. USSR, 85, 1033 (1952); N. K. Kochetkov, A. N. Nesmeyanov, and N. A. Semenov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, No. 1, 87 (T. p. 97)*; N. K. Kochetkov, A. Gonsales, and A. N. Nesmeyanov, Proc. Acad. Sci. USSR, 79, 609 (1951).

[2] H. Rupe, E. Burckhardt, Ber. 49, 2552 (1916).

[3] L. Panizzi, Gazz. chim. ital. 77, 549 (1948).

[4] A. N. Engelgardt and L. Lachinov, J. Russ. Phys. Chem. Soc., 1, 220 (1869).

[5] H. Pichtrenhain, Ber., 82, 405 (1949).

[6] F. Tiemann, H. Schotten, Ber., 11, 767 (1878).

[7] C. Schall, Ber., 12, 816 (1879).

[8] R. Stolle, W. Knebel, Ber., 54, 1213 (1921).

[9] I. Houben, W. Fischer, J. prak. Chem. [2], 123, 271 (1929).

[10] A. Pinner, Ber., 23, 2939 (1890).

[11] K. Auwers, F. Michaelis, Ber., 47, 1296 (1914).

[12] K. Niementowski, B. Rosanski, Ber., 21, 1922 (1888).

[13] T. Richards, J. Mathews, J. Am. Chem. Soc., 30, 10 (1908).

[14] F. Krollpfeiffer, Ann., 430, 202 (1923).

[15] A. Behal, E. Choay, Bull. chim. France [3], 11, 603 (1894).

[16] O. Kruber, A. Schmitt, Ber., 64, 2271 (1931).

[17] M. V. Likhosherstov, A. A. Petrov, and S. V. Alekseev, J. Gen. Chem., 4, 1277 (1934).

[18] V. Prelog, J. Wursch, K. Königsbacher, Helv. chim. acta, 34, 258 (1951).

[19] S. Cousin, F. Lions, C. A., 31, 6637 (1937).

[20] F. Eijkmaann, Chem. Weekblad, 1, 453 (1904).

Received September 15, 1954

M. V. Lomonosov State
University, Moscow

---

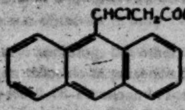
* T. p. = C. B. Translation pagination.

REACTION OF 2-CHLOROVINYL KETONES WITH ANTHRACENE

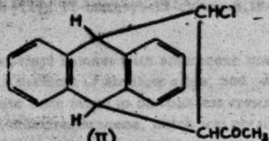
A. N. Nesmeyanov, M. I. Rybinskaya, and N. K. Kochetkov

Investigation of the ketovinylation reaction has shown that, like acid anhydrides, 2-chlorovinyl ketones condense with aromatic compounds in presence of Friedel-Crafts catalysts; in this way substituted styryl ketones may be prepared [1]. On the other hand, 2-chlorovinyl keytones readily undergo the diene-synthesis reaction with hydrocarbon dienes (cyclopentadiene, aliphatic dienes; [2, 3]. It was of interest, therefore, to determine which of these two processes would occur in the reaction between a 2-chlorovinyl ketone and anthracene since it is well known that the anthracene molecule combines within itself the properties of an aromatic compound and a diene system. It was found that, in benzene solution at room temperature, 2-chlorovinyl methyl ketone does not react with anthracene: even after a long treatment, only the original substances could be isolated from the reaction mixture. A five-hour treatment in toluene also did not give positive results.

Very different behavior was found when the reaction was carried out in presence of an equimolecular amount of stannic chloride as catalyst. A new substance was then isolated from the reaction mixture, and analysis showed that this was formed by the addition of one molecule of 2-chlorovinyl methyl ketone to one molecule of anthracene. The resulting compound contained a carbonyl group, the presence of which was confirmed by the formation of the 2,4-dinitrophenylhydrazone and the azine. Oxidation of the adduct in acetone with potassium permanganate gave anthraquinone: this indicates that it is the meso carbon atoms of anthracene that are concerned in the condensation with 2-chlorovinyl methyl ketone, for it is known that oxidation of meso-substituted anthracenes always gives anthraquinone [4, 5], whereas anthracenes substituted in the side nuclei are oxidized to the corresponding anthraquinonecarboxylic acids [6].



(I)



(II)

Hence, there was a choice of two formulas (I) and (II) for structure of the adduct, i.e. either anthracene adds, by virtue of its mobile meso hydrogen atom, to the double bond of 2-chlorovinyl methyl ketone, or diene synthesis occurs with formation of 11-acetyl-12-chloro-9,10-dihydro-9,10-ethanoanthracene. It might be thought that formula (I) should be preferred, since numerous examples are known of the addition of aromatic hydrocarbons to α,β-unsaturated ketones in presence of Friedel-Crafts catalysts [7]. However, in the course of our investigation of the adduct, we found it necessary to reject this formula and to accept formula (II). It was found, in fact, that the ultraviolet absorption spectrum of our substance (Fig. 1) is close in form to that of the adduct formed by anthracene with maleic anhydride (Fig. 2), the values of λ_{max} being almost identical (λ_{max} = 265 and 273 mμ). These absorption curves are close in form to that of 9,10-dihydroanthracene, and are quite different from those of anthracene and its meso substitution products * [9].

We can, however, advance also purely chemical arguments in favor of formula (II). Thus, under the action of caustic alkali the adduct formed by anthracene with 2-chlorovinyl methyl ketone eliminates hydrogen chloride and gives an unsaturated ketone, differing in properties from the known 4-(9-anthryl)-3-buten-2-one [10], the formation of which would be expected if the formula of the adduct is (I).

---

* The absorption curves were determined with a Dianov-Klokov spectrophotometer [8] in the Laboratory for Physico-chemical Investigation of Organic Compounds of the Organic Chemistry Department of the Moscow State University.

The condensation of 2-chlorovinyl ketones with anthracene was found to be fairly general. The reaction was carried out also on propyl, pentyl, and phenyl 2-chlorovinyl ketones. Reaction of these with anthracene in presence of stannic chloride in a medium of absolute benzene gave the corresponding adducts in yields of 70-84%.

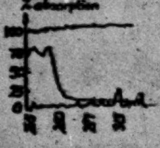


Fig. 1

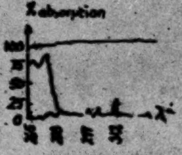
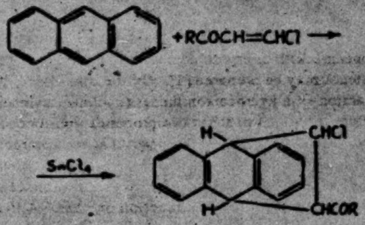


Fig. 2

Fig. 1. Ultraviolet absorption spectrum of the adduct formed by 2-chlorovinyl methyl ketone with anthracene (in dichloroethane solution).

Fig. 2. Ultraviolet absorption spectrum of the adduct formed by maleic anhydride with anthracene (in dichloroethane solution).

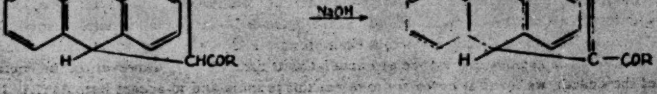


in which R = CH_3-, C_3H_7-, $C_5H_{11}-$, C_6H_5-

The 11-acyl-12-chloro-9,10-dihydro-9,10-ethanoanthracenes obtained in this way were found to be colorless crystalline substances which decompose with separation of anthracene when heated to 200°.

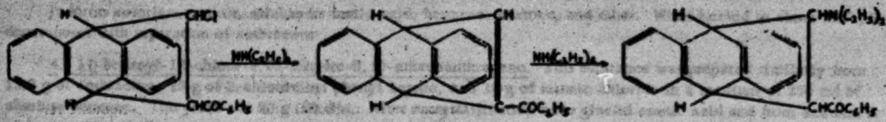
It must be emphasized that the diene condensation of 2-chlorovinyl ketones with anthracene will occur – and then, very readily – only in the presence of stannic chloride, although it is probable that other Friedel-Crafts catalysts could be used in our reaction. It is interesting that, when 2-chlorovinyl phenyl ketone was treated with anthracene in boiling xylene with passage of hydrogen chloride (as recommended by Barnett for the preparation of adducts of α,β-unsaturated ketones with anthracene [11]), 11-benzoyl-12-chloro-9,10-dihydro-9,10-ethanoanthracene was obtained in only 17% yield.

Like the methyl homolog, the other adducts of alkyl 2-chlorovinyl ketones with anthracene smoothly eliminated hydrogen chloride in presence of solid caustic soda in a medium of absolute ether, and good yields of 11-acyl-9,10-dihydro-9,10-ethenoanthracenes were obtained. These were found to be colorless crystalline substances, with the exception of 11-hexanoyl-9,10-dihydro-9,10-ethenoanthracene, which was obtained as a viscous noncrystallizing oil.



in which R = CH_3-, C_3H_7-, C_6H_5-

It is interesting that, under these conditions, the adduct formed by 2-chlorovinyl phenyl ketone with anthracene eliminates hydrogen chloride very slowly, the result of the reaction being a mixture of the original substance and unsaturated ketone, which is difficult to separate. With the object of isolating the pure unsaturated ketone, 11-benzoyl-12-chloro-9,10-dihydro-9,10-ethanoanthracene was boiled for two hours in diethylamine solution. The homogeneity of the medium then ensured the smooth elimination of hydrogen chloride, but it was found that the diethylamine itself reacted with some of the product by addition at the double bond, and the final product was a mixture of 11-benzoyl-9,10-dihydro-9,10-ethenoanthracene (26.7% yield) and 11-benzoyl-12-diethylamino-9,10-dihydro-9,10-ethanoanthracene (64.3% yield):



Treatment of the adduct formed by 2-chlorovinyl methyl ketone with alcoholic alkali yielded 11-acetyl-12-ethoxy-9,10-dihydro-9,10-ethanoanthracene. It is probable that here again the unsaturated ketone is formed in the first stage, and this then readily combines with an alcohol molecule at the double bond.

EXPERIMENTAL

1. 11-Acetyl-12-chloro-9,10-dihydro-9,10-ethanoanthracene. Stannic chloride (19 g) was added dropwise over a period of one hour to a vigorously-stirred mixture of 12.8 g of anthracene, 7.5 g of 2-chlorovinyl methyl ketone, and 200 ml of absolute benzene; The addition of the first few drops of stannic chloride caused the reaction mixture to turn brown. The whole of the anthracene gradually dissolved, and a fine precipitate of the complex formed. When the whole of the stannic chloride had been added, the mixture was stirred for a further five hours and then decomposed by adding dilute hydrochloric acid while cooling the reaction flask with ice water. The benzene layer was separated, washed several times with water, then washed with sodium carbonate solution, and then again with water. The solution was dried over calcium chloride, benzene was distilled off under reduced pressure, and the solid residue was recrystallized from acetic acid. Yield 17.8 g (87.6%); m.p. 147°.

Found %: C 76.11; 76.04; H 5.44; 5.35; Cl 12.40; 12.48
$C_{18}H_{15}OCl$. Calculated %: C 76.48; H 5.31; Cl 12.46

The substance forms colorless plates, readily soluble in hot acetic acid, in benzene, and in acetone. When heated to 200° it decomposes with separation of anthracene.

The azine was prepared by reaction with an alcoholic solution of hydrazine. It is a colorless powder, insoluble in most organic solvents; m.p. 162-164° (decomp.).

Found %: N 5.29; 5.19
$C_{36}H_{30}N_2Cl_2$. Calculated %: N 5.00

The 2,4-dinitrophenylhydrazone was prepared in a medium of glacial acetic acid and was recrystallized from the same solvent. It forms orange crystals, m.p. 278°.

Found %. N 12.22; 12.29
$C_{24}H_{19}O_4N_4Cl$. Calculated %: N 12.11

2. 11-Butyryl-12-chloro-9,10-dihydro-9,10-ethanoanthracene. This substance was prepared similarly from 17 g of anthracene, 15.5 g of 2-chlorovinyl propyl ketone, and 25 g of stannic chloride in a medium of 250 ml of absolute benzene. The yield was 25 g (84.4%). After recrystallization, first from acetic acid, and then from absolute acetone, it melted at 93-94°.

Found %: C 77.64; H 6.13; Cl 11.57
$C_{20}H_{19}OCl$. Calculated %: C 77.28; H 6.16; Cl 11.40

It forms colorless crystals, readily soluble in hot acetic acid, in benzene, in acetone, and in ether. When heated to about 200°, it decomposes with separation of anthracene.

3. 11-Hexanoyl-12-chloro-9,10-dihydro-9,10-ethanoanthracene. This substance was prepared similarly from 15 g of anthracene, 15 g of 2-chlorovinyl pentyl ketone, and 25 g of stannic chloride in 250 ml of absolute benzene. The solid residue remaining after removal of benzene was pressed out on a porous plate. The yield was 20 g (70.1%). After

recrystallization, first from glacial acetic acid, and then from acetone, it melted at 82°.

Found %: C 77.91; 78.11; H 6.85; 6.96; Cl 10.37; 10.66
$C_{22}H_{23}OCl$. Calculated %: C 77.97; H 6.84; Cl 10.41

It forms colorless crystals, soluble in acetic acid, benzene, acetone, and ether. When heated to about 200°, it decomposes with separation of anthracene.

4. 11-Benzoyl-12-chloro-9,10-dihydro-9,10-ethanoanthracene. This substance was prepared similarly from 12.8 g of anthracene, 12 g of 2-chlorovinyl phenyl ketone, and 19 g of stannic chloride in a medium of 200 ml of absolute benzene. The yield was 20 g (80.6%). After recrystallization from glacial acetic acid and from acetone it melted at 184-186°.

Found %: C 80.08; 80.11; H 5.18; 5.03
$C_{23}H_{17}OCl$. Calculated %: C 80.10; H 4.96

It forms colorless crystals, soluble in acetic acid, toluene, and acetone.

5. Reaction of 2-Chlorovinyl Phenyl Ketone with Anthracene in Presence of Hydrogen Chloride. 2-Chlorovinyl phenyl ketone (6 g) was added to a suspension of 3 g of anthracene in 50 ml of absolute o-xylene. The mixture was boiled, and a stream of dry hydrogen chloride was passed through for ten hours. The undissolved anthracene was filtered off, and the filtrate was evaporated by heating it under reduced pressure (5 mm). Recrystallization of the residue from acetic acid yielded 1 g (16.8%) of adduct, m.p. 183-185°. In a mixture melting point test with 11-benzoyl-12-chloro-9,10-dihydro-9,10-ethanoanthracene there was no depression.

6. 11-Acetyl-9,10-dihydro-10-ethenoanthracene. Finely ground caustic soda (6 g) was added to a solution of 3 g of 11-acetyl-12-chloro-9,10-dihydro-9,10-ethanoanthracene in 100 ml of absolute ether, and the mixture was shaken vigorously for ten hours. The solution was then filtered and evaporated under reduced pressure. The solid residue was recrystallized from absolute acetone; yield 2 g (76.9%); m.p. 174-175°.

Found %: C 87.77; 87.57; H 5.78; 5.88
$C_{18}H_{14}O$. Calculated %: C 87.80; H 5.75

The substance forms colorless crystals, soluble in ether, acetone, and benzene.

7. 11-Butyryl-9,10-dihydro-9,10-ethenoanthracene. This was prepared similarly by treatment of 2 g of 11-butyryl-12-chloro-9,10-dihydro-9,10-ethanoanthracene with 6 g of finely ground caustic soda in 100 ml of absolute ether. The yield was 1.4 g (79.5%). After recrystallization from dry acetone it melted at 151-153°.

Found %: C 87.78; 87.57; H 6.50; 6.55
$C_{20}H_{18}O$. Calculated %: C 87.55; H 6.61

The substance forms colorless crystals, soluble in ether, benzene, and acetone.

8. 11-Hexanoyl-9,10-dihydro-9,10-ethenoanthracene. This was prepared similarly by treatment of 3 g of 11-hexanoyl-12-chloro-9,10-dihydro-9,10-ethanoanthracene with 10 g of finely ground caustic soda in 50 ml of absolute ether. The residue after removal of ether was a noncrystallizing viscous oil, which was dried under reduced pressure (7 mm) at 80° in presence of phosphoric oxide. Yield 2.5 g (96%); n_D^{25} 1.5900.

Found %: C 87.11; H 7.30
$C_{22}H_{22}O$. Calculated %: C 87.37; H 7.25

9. Reaction of 11-Benzoyl-12-chloro-9,10-dihyrdo-9,10-ethanoanthracene with Diethylamine. 11-Benzoyl-12-chloro-9,10-dihydro-9,10-ethanoanthracene (3.3 g) was added to 50 ml of diethylamine, and the mixture was refluxed for two hours and then set aside for one day at room temperature. The excess of diethylamine was then distilled off, 100-150 ml of 5% hydrochloric acid was added to the residue, and the resulting mixture was extracted with ether (the aqueous layer was kept). The ether extract was washed several times with 5% hydrochloric acid and then with water (the washings were added to the hydrochloric acid solution). After being dried over sodium sulfate, the ether layer was distilled, and yielded 0.77 g (26.3%) of 11-benzoyl-9,10-dihydro-9,10-ethenoanthracene, m.p. 162-163° after recrystallization from dry acetone.

Found %: C 89.62; 89.59; H 5.36; 5.27
$C_{23}H_{16}O$. Calculated %: C 89.59; H 5.23

The hydrochloric acid solution was extracted several times with ether, and then 10% caustic soda was added until a white precipitate separated. The precipitate was rapidly filtered off, washed with water, and twice reprecipitated with alkali from solution in 5% hydrochloric acid. The yield of 11-benzoyl-12-diethylamino-9,10-dihydro-9,10-ethanoanthracene was 2.35 g (64.3%). After recrystallization from aqueous methanol it melted at 52-54°.

The substance forms a difficultly crystallizable yellowish powder, readily soluble in alcohol, ether, acetone, and petroleum ether.

Its picrate was prepared in methanol and recrystallized from the same solvent: lemon-yellow needles, m.p. 187-188°.

Found %: N 9.39; 9.54

$C_{33}H_{30}O_8N_4$. Calculated %: N 9.18

10. 11-Acetyl-12-ethoxy-9,10-dihydro-9,10-ethanoanthracene. A mixture of 0.86 g of 11-acetyl-12-chloro-9,10-dihydro-9,10-ethanoanthracene, 0.6 g of caustic soda, and 15 ml of ethanol was shaken at room temperature for three hours. A precipitate of sodium chloride formed. The reaction mixture was poured into 70 ml of water. The white precipitate that separated was filtered off and washed on the filter with several successive portions of water. The yield was 0.8 g (87.8%). After recrystallization from acetone it melted at 162-164°.

Found %: C 82.36; H 6.90

$C_{20}H_{20}O_2$. Calculated %: C 82.19; H 6.90

SUMMARY

1. 2-Chlorovinyl ketones react with anthracene in accordance with the scheme of the diene synthesis.

2. It is shown for the first time that stannic chloride is a catalyst for the diene-synthesis reaction.

3. The 11-acyl-12-chloro-9,10-dihydro-9,10-ethanoanthracenes formed in this reaction are reactive substances and can be used as starting materials for the synthesis of various 9,10-ethanoanthracene derivatives.

LITERATURE CITED

[1] A. N. Nesmeyanov, N. K. Kochetkov, and L. A. Matov, Proc. Acad. Sci. USSR, 92, 85 (1953).

[2] A. N. Nesmeyanov, N. K. Kochetkov, M. Ya. Karpeisky, and G. V. Aleksandrova, Proc. Acad. Sci. USSR, 82, 409 (1952).

[3] N. K. Kochetkov and G. V. Aleksandrova, Proc. Acad. Sci. USSR, 85, 1033 (1952).

[4] E. Martin, Ann. Combustibles liquides, 12, 97 (1927); C. A. 31, 3908 (1937).

[5] O. Diels, K. Alder, S. Beekman, Ann. 486, 191 (1931).

[6] M. A. Ilyinsky and V. A. Kazakova, J. Gen. Chem., 11, 16 (1941).

[7] D. Vorländer, A. Friedberg, Ber, 56, 1144 (1923).

[8] V. I. Dianov- Klokov, Factory Labs., 3, 361 (1955); 5, 614 (1955).

[9] R. A. Friedel, M. Orchin, Ultraviolet Spectra of Aromatic Compounds 114, 338, 229 (1951).

[10] A. Mustafa, Science 112, 440 (1950); C. A. 45 , 4231 (1951).

[11] E. B. Barnett, N. F. Goodway, E. V. Weeks, J. Chem. Soc. 1935, 1102.

M. V. Lomonosov State University
Moscow

Received September 24, 1954

BLANK
PAGE

DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 10. DIESTERS OF 2-ALKOXY- AND 2-PHENOXY-VINYLPHOSPHONODITHIOLIC AND OF 2-ALKOXY- AND 2-PHENOXY-VINYL PHOSPHONOTRITHIOIC ACIDS

K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov

Possible methods for the synthesis of diesters of 2-alkoxy- and 2-phenoxy-vinylphosphonodithiolic acids are 1) the action of 2-alkoxy- and 2-phenoxy-vinylphosphonic dichlorides on thiols in the presence of pyridine, and 2) the action of 2-alkoxy- and 2-phenoxy-vinylphosphonic dichlorides on sodium mercaptides.

The first reaction proved to be satisfactory only in the preparation of S,S-diphenyl 2-isobutoxyvinylphosphonodithioate; in all other cases we were unable to isolate the substance in the pure state, since it decomposed during vacuum distillation. By the second method, which has been extensively used by A. E. Arbuzov [1], we were able to prepare the diethyl esters of 2-ethoxy-, 2-butoxy-, 2-isobutoxy, and 2-phenoxy-vinylphosphonodithiolic acids. These compounds are slightly yellow liquids which can be readily distilled under reduced pressure. They are soluble in the usual organic solvents, but insoluble in water. Table 1 gives the constants of the esters obtained.

We prepared diesters of 2-alkoxy- and 2-phenoxy-vinylphosphonotrithioic acids by a method analogous to the second method. These esters are thick yellowish liquids. They are readily soluble in organic solvents, but are insoluble in water. Properties of these esters are given in Table 2.

TABLE 1

Formula of substance	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}
$C_2H_5-O-CH=CHPO(S-C_2H_5)_2$.	135 (2)	1.5475	1.1366
$n\text{-}C_4H_9-O-CH=CHPO(S-C_2H_5)_2$	154 (2)	1.5544	1.1410
$i\text{-}C_4H_9-O-CH=CHPO(S-C_2H_5)_2$	145 (2)	1.5370	1.0961
$i\text{-}C_4H_9-O-CH=CHPO(S-C_6H_5)_2$	m.p. 72–73		
$C_6H_5-O-CH=CHPO(S-C_2H_5)_2$	162 (1)	1.5860	1.1535

TABLE 2

Formula of substance	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}
$C_2H_5-O-CH=CHPS(S-C_2H_5)_2$	134 (1)	1.5858	1.1734
$i\text{-}C_3H_7-O-CH=CHPS(S-C_2H_5)_2$	136 (2)	1.5672	1.1198
$i\text{-}C_4H_9-O-CH=CHPS(S-C_2H_5)_2$	145 (1)	1.5662	1.1060
$C_6H_5-O-CH=CHPS(S-C_2H_5)_2$	155 (1)	1.6336	1.3142

EXPERIMENTAL

S,S-Diethyl 2-Ethoxyvinylphosphonodithioate $C_2H_5-O-CH=CHPO(SC_2H_5)_2$. Sodium (2.3 g) was prepared for reaction by Brühl's method and added to 150 ml of absolute ether; the mixture was cooled while 9 g of ethanethiol was added. On the next day a solution of 9.45 g of 2-ethoxyvinylphosphonic dichloride in an equal volume of ether was added with stirring. When reaction was complete, the ether layer was poured off and dried over calcined sodium sulfate. The ether was distilled off, and vacuum fractionation of the residue gave 6.7 g (55.8%) of product. After the third fractionation it had b.p. 135° (2 mm); n_D^{20} 1.5475; d_4^{20} 1.1366.

Found %: P 12.75; 12.77

$C_8H_{17}O_2S_2P$. Calculated %: P 12.91

S,S-Diethyl 2-Butoxyvinylphosphonodithioate n-$C_4H_9-O-CH=CHPO(SC_2H_5)_2$. Sodium wire (2 g) was added to 150 ml of absolute ether contained in a three-necked flask fitted with stirrer. The flask was cooled, and a solution of 9 g of ethanethiol in an equal volume of ether was added slowly from a dropping funnel. When the whole of the thiol had been added, a few pieces of sodium were introduced into the flask and the reaction mixture was set aside overnight. On the next day the mixture was heated for two hours at 30° in a water bath and the pieces of sodium were removed. The mixture was cooled, and a solution of 11.85 g of 2-butoxyvinylphosphonic dichloride in 15 ml of ether was added. When reaction was complete, the ether layer was poured off, the precipitate was washed twice with ether, and the filtrate was dried over sodium sulfate and vacuum-fractionated: b.p. 154° (2 mm); d_4^{20} 1.1410; n_4^{20} 1.5544; yield 7.6 g (52 %).

Found %: P 11.47; 11.58
$C_{10}H_{21}O_2S_2P$. Calculated %: P 11.56

S,S-Diethyl 2-Isobutoxyvinylphosphonodithioate i-$C_4H_9-O-CH=CHPO(SC_2H_5)_2$. 2-Isobutoxyvinylphosphonic dichloride (11.85 g) was added with stirring and cooling to sodium mercaptide prepared in absolute ether from 2.3 g of Brühl sodium and 9 g of ethanethiol. The product isolated amounted to 9 g (63%) and had b.p. 145° (2 mm); n_D^{20} 1.5370; d_4^{20} 1.0961.

Found %: P 11.34; 11.41
$C_{10}H_{21}O_2S_2P$. Calculated %: P 11.56

S,S-Diphenyl 2-Isobutoxyvinylphosphonodithioate i-$C_4H_9-O-CH=CHPO(SC_6H_5)_2$. Pyridine (7.2 g) and benzenethiol (10 g) were added to 150 ml of dry benzene, and the resulting mixture was stirred and cooled slightly while a solution of 10 g of 2-isobutoxyvinylphosphonic dichloride in 10 ml of benzene was added from a dropping funnel over a period of one hour. When the whole of the acid chloride had been added the mixture was set aside overnight. On the next day the precipitate of pyridine hydrochloride was filtered off. The filtrate was treated with 3% sodium carbonate solution and dried with sodium sulfate. Benzene was distilled off, and 12 g of crude crystalline product was isolated. Recrystallization from petroleum ether gave 10 g (60%) of pure product, m.p. 72-73°.

Found %: C 59.43; 59.49; H 5.93; 6.09
$C_{18}H_{21}O_2PS_2$. Calculated %: C 59.34 H 5.77

S,S-Diethyl 2-Phenoxyvinylphosphonodithioate $C_6H_5-O-CH=CHPO(SC_2H_5)_2$. A solution of 9.5 g of ethanethiol in 20 ml of ether was added gradually to a cooled slowly stirred mixture of 2.3 g of Brühl sodium and 200 ml of absolute ether contained in a three-necked flask. The resulting mercaptide was left overnight. On the next day 11.85 g of 2-phenoxyvinylphosphonic dichloride was added with stirring. When reaction was complete the ether layer was poured off. The filtrate was dried over calcined sodium sulfate and fractionated. The product, amounting to 9 g, had b.p. 162° (1 mm); n_D^{20} 1.5860; d_D^{20} 1.1535.

Found %: P 10.55; 10.74
$C_{12}H_{17}O_2S_2P$. Calculated %: P 10.76

Diethyl 2-Ethoxyvinylphosphonotrithioate $C_2H_5-O-CH=CH-PS(SC_2H_5)_2$. Brühl sodium (2.3 g) was added to absolute ether contained in a three-necked flask fitted with stirrer, reflux condenser, and dropping funnel. With cooling and slow stirring, a solution of 9.5 g of ethanethiol in an equal volume of ether was added. On the next day the mixture was heated for one hour at 30-35° in a water bath, and to the sodium ethylmercaptide so formed 10.2 g of 2-ethoxyvinylphosphonothioic dichloride was added from a dropping funnel. When addition of the acid chloride was complete, the mixture was set aside overnight and then heated at 30-35° for two hours. The precipitate was filtered off, and the filtrate was dried over calcined sodium sulfate. After removal of ether the residue was vacuum-fractionated and yielded 8.4 g (65.9%) of substance of b.p. 134° (1 mm); n_D^{20} 1.5858; d_4^{20} 1.1734.

Found %: C 37.46; 37.21; H 6.41; 6.29
$C_8H_{17}OPS_3$ Calculated %: C 37.50; H 6.50

Diethyl 2-Isopropoxyvinylphosphonotrithioate $i\text{-}C_3H_7-O-CH=CH-PS(SC_2H_5)_2$. A solution of 10.95 g of 2-isopropoxyvinylphosphonothioic dichloride in 15 ml of ether was added to sodium ethylmercaptide, prepared from 2.3 g of sodium and 9 g of ethanethiol in 300 ml of absolute ether. When the whole of the acid chloride had been added, the reaction mixture was set aside overnight. On the next day the mixture was heated in a water bath at 30° and the ether layer was poured off. The filtrate was dried over sodium sulfate. The product, amounting to 8 g (59.2%), had b.p. 136° (2 mm); n_D^{20} 1.5672; d_4^{20} 1.1190.

Found %: C 40.09; 40.34 H 6.48; 6.73
$C_9H_{19}OPS_3$. Calculated %: C 40.00; H 7.03

Diethyl 2-Isobutoxyvinylphosphonotrithioate $i\text{-}C_4H_9-O-CH=CHPS(SC_2H_5)_2$. Sodium ethylmercaptide, prepared from 9 g of ethanethiol and 2.3 g of Brühl sodium, was placed in a flask, and 11.65 g of 2-butoxyvinylphosphonothioic dichloride was added gradually over a period of two hours. The reaction mixture was then set aside overnight. On the next day the mixture was warmed, and the ether layer was poured off and vacuum-fractionated. The yield of pure product was 8.6 g (60%), and it had b. p. 145° (1 mm); n_D^{20} 1.5662; d_4^{20} 1.1060.

Found %: C 42.63; 42.76; H 7.27; 7.36
$C_{10}H_{21}OPS_3$. Calculated %: C 42.25; H 7.39

Diethyl 2-Phenoxyvinylphosphonotrithioate $C_6H_5-O-CH=CHPS(SC_2H_5)_2$. A solution of 12.65 g of 2-phenoxyvinylphosphonothioic dichloride in 15 ml of absolute ether was added with stirring and cooling to sodium ethylmercaptide, prepared from 2.3 g of sodium and 9.5 g of ethanethiol in 250 ml of absolute ether. When the whole of the acid chloride had been added, the reaction mixture was set aside overnight. On the next day the mixture was warmed at 20° for two hours, and the ether layer was poured off and vacuum-fractionated. The product, amounting to 7.2 g (47%), had b.p. 155° (1 mm); n_D^{20} 1.6336; d_4^{20} 1.3142.

Found %: P 10.40; 10.27
$C_{12}H_{17}OPS_3$. Calculated %: P 10.19

SUMMARY

1. By the action of 2-ethoxy-, 2-butoxy-, 2-isobutoxy-, and 2-phenoxy-vinylphosphonic dichlorides on sodium ethylmercaptide, the diethyl esters of the corresponding 2-alkoxy-and 2-phenoxy-vinylphosphonodithiolic acids were prepared.

2. The diethyl esters of 2-ethoxy-, 2-isopropoxy-, 2-isobutoxy-, and 2-phenoxy-vinylphosphonotrithioic acids were synthesized by the reaction of sodium ethylmercaptide with the corresponding phosphonothioic dichlorides.

3. S,S-Diphenyl 2-isobutoxyvinylphosphonodithioate was prepared by the action of 2-isobutoxyvinylphosphonic dichloride on benzenethiol in presence of pyridine.

Received April 11, 1954

Institute of Heteroorganic Compounds
of the USSR Academy of Sciences

LITERATURE CITED

[1] A. E. Arbuzov, Selected Works, Acad. Sci. USSR Press, Moscow, 1952. p. 225.

DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 11. DIESTERS OF 2-(2-ALKOXYETHOXY)VINYLPHOSPHONIC ACIDS

K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov

We prepared diesters of 2-(2-alkoxyethoxyl)vinylphosphonic acids by reaction of acid chlorides with alcohols in presence of pyridine in a benzene medium, following the method of Milobendzsky and Sakhnovsky [1]:

$$ROCH_2-CH_2-O-CH=CHPOCl_2 + 2ROH + 2C_5H_5N =$$
$$= ROCH_2-CH_2-O-CH=CHPO(OR)_2 + 2C_5H_5 \cdot N \cdot HCl.$$

By this method we prepared the dimethyl, diethyl, dipropyl, diisopropyl, dibutyl, diisobutyl, diallyl, dihexyl, diheptyl, bis(2-methoxyethyl), and bis(2-ethoxyethyl) esters of 2-(2-methoxyethoxy)-, 2-(2-ethoxyethoxy)-, and 2-(2-butoxyethoxy)-vinyl-phosphonic acids in yields of up to 88%. The diesters of 2-(2-alkoxyethoxy)vinylphosphonic acids are colorless liquids that can be readily distilled under reduced pressure. They are soluble in many organic solvents, and some are soluble in water. Tables 1-3 give the constants of the esters we have synthesized.

TABLE 1

Formula of substance	B.p. °C (p in mm)	n_D^{20}	d_4^{20}	Yield (%)
$CH_3-O-CH_2-CH_2-O-CH=CHPO(OCH_3)_2$	124 (1)	1.4590	1.1747	77.9
$CH_3-O-CH_2-CH_2-O-CH=CHPO(OC_2H_5)_2$	134 (1)	1.4525	1.1067	76
$CH_3-O-CH_2-CH_2-O-CH=CHPO(OC_3H_7\text{-}n)_2$	143 (1)	1.4510	1.0585	88
$CH_3-O-CH_2-CH_2-O-CH=CHPO(OC_3H_7\text{-}i)_2$	134 (2)	1.4469	1.0529	77
$CH_3-O-CH_2-CH_2-O-CH=CHPO(OC_4H_9\text{-}n)_2$	153 (1)*	1.4518	1.0354	75
$CH_3-O-CH_2-CH_2-O-CH=CHPO(OC_4H_9\text{-}i)_2$	148 (1)	1.4500	1.0341	77
$CH_3-O-CH_2-CH_2-O-CH=CHPO(OC_3H_5)_2$	160 (2)	1.4789	1.1082	80
$CH_3-O-CH_2-CH_2-O-CH=CHPO(OC_6H_{13}\text{-}n)_2$	180 (1)	1.4540	1.0004	80
$CH_3-O-CH_2-CH_2-O-CH=CHPO(OC_7H_{15}\text{-}n)_2$	190 (1)	1.4562	0.9845	62
$CH_3-O-CH_2-CH_2-O-CH=CHPO(OCH_2-$ $-CH_2OCH_3)_2$	171 (1)	1.4620	1.1467	70
$CH_3-O-CH_2-CH_2-O-CH=CHPO(OCH_2-CH_2-$ $-OC_2H_5)_2$	175 (1)	1.4570	1.1088	76

TABLE 2

Formula of substance	B.p. °C (p in mm)	n_D^{20}	d_4^{20}	Yield (%)
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OCH_3)_2$	126 (2)	1.4528	1.1429	76
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OC_2H_5)_2$	133.5 (2)	1.4512	1.0812	78
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OC_3H_7\text{-}n)_2$	140 (2)	1.4510	1.0470	80
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OC_3H_7\text{-}i)_2$	125 (2)	1.4452	1.0341	72
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OC_4H_9\text{-}i)_2$	143 (2)	1.4492	1.0159	82
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OC_3H_5)_2$	138.5 (2)	1.4702	1.0854	77
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OC_7H_{15}\text{-}n)_2$	200 (1)	1.4546	0.9745	88
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OCH_2-CH_2-$ $-OCH_3)_2$	163 (1)	1.4602	1.1279	84
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OCH_2-CH_2-$ $-OC_2H_5)_2$	180 (1)	1.4546	1.0917	86

TABLE 3

Formula of substance	B.p., °C (p in mm)	n_D^{20}	d_4^{20}	Yield (%)
$n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO(OCH_3)_2$	132 (1)	1.4565	1.1100	77
$n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO(OC_2H_5)_2$	155 (2)	1.4519	1.0815	79
$n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO(OC_3H_7\text{-}n)_2$	163 (2)	1.4529	1.0199	83
$n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO(OC_4H_9\text{-}n)_2$	180 (2)	1.4532	1.0008	86
$n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO(O-C_4H_9\text{-}i)_2$	172 (2)	1.4512	1.0002	83
$n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO(OC_6H_5)_2$	152 (1)	1.4860	1.0530	71
$n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO(OC_6H_{13}\text{-}n)_2$	202 (2)	1.4550	0.9794	85
$n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO(OC_7H_{15}\text{-}n)_2$	207 (1)	1.4553	0.9644	89
$n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO(OCH_2-$ $-CH_2-O-C_2H_5)_2$	193 (2)	1.4561	1.0643	87

EXPERIMENTAL

2-(2-Methoxyethoxy)vinylphosphonic Esters

Dimethyl 2-(2-Methoxyethoxy)vinylphosphonate $CH_3-O-CH_2-CH_2-O-CH=CHPO(OCH_3)_2$. A mixture of 100 ml of dry benzene, 8.5 g of absolute methanol, and 8 g of pyridine was prepared in a flask fitted with stirrer, reflux condenser, and dropping funnel. With stirring and cooling, 10.85 g of 2-(2-methoxyethoxy)vinylphosphonic dichloride was added gradually. On the next day pyridine hydrochloride was filtered off, and the filtrate was washed with 3% sodium carbonate solution and dried over sodium sulfate. Vacuum fractionation yielded 8.5 g of substance (79% yield) having b.p. 124° (1 mm); n_D^{20} 1.4590; d_4^{20} 1.1747.

Found %: P 14.56; 14.60

$C_7H_{15}O_5P$. Calculated %: P 14.76

The preparation of the other esters was similar to that of dimethyl 2-(2-methoxyethoxy)vinylphosphonate.

Diethyl 2-(2-Methoxyethoxy)vinylphosphonate $CH_3-O-CH_2-CH_2-O-CH=CHPO(OC_2H_5)_2$. To a stirred cooled mixture of 5 g of absolute ethanol, 8 g of pyridine, and 80 ml of dry benzene, 10.95 g of 2-(2-methoxyethoxy)-vinylphosphonic dichloride was added. The product, amounting to 9 g (76%), had b.p. 134° (1 mm); n_D^{20} 1.4525; d_4^{20} 1.1067.

Found %: P 12.97; 13.00

$C_9H_{19}O_5P$. Calculated %: P 13.02

Dipropyl 2-(2-Methoxyethoxy)vinylphosphonate $CH_3-O-CH_2-CH_2-O-CH=CHPO(OC_3H_7\text{-}n)_2$. 2-(2-Methoxyethoxy)vinylphosphonic dichloride (12 g) was added with stirring to a mixture of 100 ml of dry benzene, 8.6 g of pyridine, and 6.6 g of absolute propyl alcohol. The product amounting to 12.9 g (88%), had b.p. 143° (1 mm); n_D^{20} 1.4510; d_4^{20} 1.0585.

Found %: P 11.54; 11.34

$C_{11}H_{23}O_5P$. Calculated %: P 11.65

Diisopropyl 2-(2-Methoxyethoxy)vinylphosphonate $CH_3-O-CH_2-CH_2-O-CH=CHPO(OC_3H_7\text{-}i)_2$. A solution of 15 g of 2-(2-methoxyethoxy)vinylphosphonic dichloride in 15 ml of benzene was added to a mixture of 8.5 g of absolute isopropyl alcohol and 11 g of pyridine. The product, amounting to 14.5 g (77%), had b.p. 134° (2 mm); n_D^{20} 1.4469; d_4^{20} 1.0529.

Found %: P. 11.39; 11.33

$C_{11}H_{23}O_5P$. Calculated %: P 11.65

Dibutyl 2-(2-Methoxyethoxy)vinylphosphonate $CH_3-O-CH_2-CH_2-O-CH=CHPO(OC_4H_9\text{-}n)_2$. 2-(2-Methoxyethoxy)vinylphosphonic dichloride (10.95 g) was added to a mixture of 7.4 g of absolute butyl alcohol and 8 g of pyridine. Vacuum fractionation yielded 12 g (80%) of a substance having b.p. 153° (1 mm); n_D^{20} 1.4518; d_4^{20} 1.0354.

Found %: P 10.27; 10.54

$C_{13}H_{27}O_5$. Calculated %: P 10.54

Diisobutyl 2-(2-Methoxyethoxy)vinylphosphonate $CH_3-O-CH_2-CH_2-O-CH=CHPO(O-C_4H_9\text{-}i)_2$. 2-(2-Methoxyethoxy)vinylphosphonic dichloride (12 g) was added to a mixture of 8.5 g of absolute isobutyl alcohol, 8.6 g of dry pyridine, and 80 ml of benzene. The product, amounting to 12.5 g (77%), had b.p. 148° (1 mm); n_D^{20} 1.4500; d_4^{20} 1.0341.

Found %: P 10.52; 10.55

$C_{13}H_{27}O_5P$. Calculated %: P 10.54

Diallyl 2-(2-Methoxyethoxy)vinylphosphonate $CH_3-O-CH_2-CH_2-O-CH=CHPO(OC_3H_5)_2$. 2-(2-Methoxyethoxy)vinylphosphonic dichloride (9 g) was added to a mixture of 4.8 g of absolute allyl alcohol and 7 g of pyridine. The product, amounting to 8 g, had b.p. 160° (2 mm); n_D^{20} 1.4789; d_4^{20} 1.1082.

Found %: P. 11.36; 11.41

$C_{11}H_{19}O_5P$. Calculated %: P 11.45

Dihexyl 2-(2-Methoxyethoxy)vinylphosphonate $CH_3-O-CH_2-CH_2-O-CH=CHPO(OC_6H_{13}\text{-}n)_2$. 2-(2-Methoxyethoxy)vinylphosphonic dichloride (10.95 g) was added to a mixture of 10.3 g of absolute hexyl alcohol, 8 g of pyridine, and 120 ml of dry benzene. The product, amounting to 14 g (80%), had b.p. 180° (1 mm); n_D^{20} 1.4540; d_4^{20} 1.0004.

Found %: P 8.71; 8.56

$C_{17}H_{35}O_5P$. Calculated %: P 8.85

Diheptyl 2-(2-Methoxyethoxy)vinylphosphonate $CH_3-O-CH_2-CH_2-O-CH=CHPO(OC_7H_{15}\text{-}n)_2$. 2-(2-Methoxyethoxy)vinylphosphonic dichloride (7.5 g) was added to a mixture of 8.5 g of absolute heptyl alcohol, 5.5 g of pyridine, and 100 ml of benzene. Vacuum fractionation yielded 9.3 g (79%) of product, b.p. 190° (1 mm); n_D^{20} 1.4562; d_4^{20} 0.9845.

Found %: C 59.93; 59.86; H 10.36; 10.52

$C_{19}H_{39}O_5P$. Calculated %: C 60.31; H 10.31

Bis(2-ethoxyethyl) 2-(2-Methoxyethoxy)vinylphosphonate $CH_3-O-CH_2-CH_2-O-CH=CHPO(OCH_2-CH_2-\\-OC_2H_5)_2$. 2-(2-Methoxyethoxy)vinylphosphonic dichloride (15 g) was added to a mixture of 12.5 g of 2-ethoxyethanol, 11 g of pyridine, and 120 ml of dry benzene. Vacuum fractionation yielded 17 g (76%) of product, b.p. 175° (1 mm); n_D^{20} 1.4570; d_4^{20} 1.1088.

Found %: P 9.48; 9.32

$C_{13}H_{27}O_7P$. Calculated %: P 9.50

2-(2-Ethoxyethoxy)vinylphosphonic Esters

Dimethyl 2-(2-Ethoxyethoxy)vinylphosphonate $C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OCH_3)_2$. 2-(2-Ethoxyethoxy)vinylphosphonic dichloride (9 g) was added to a mixture of 2.5 g of absolute methanol, 6.2 g of pyridine, and 60 ml of dry benzene. The product, amounting to 6.6 g (76%), had b.p. 126° (2 mm); n_D^{20} 1.4528; d_4^{20} 1.1429.

Found %: C 42.47; 42.60; H 7.69; 7.64

$C_8H_{17}O_5P$. Calculated %: C 42.85 H 7.58

Diethyl 2-(2-Ethoxyethoxy)vinylphosphonate $C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OC_2H_5)_2$. Reaction between 11.65 g of 2-(2-ethoxyethoxy)vinylphosphonic dichloride, 8 g of pyridine, and 5 g of absolute ethanol yielded 9.8 g (78%) of product, b.p. 133.5°, (2 mm); n_D^{20} 1.4512; d_4^{20} 1.0812.

Found %: C 47.09; 47.08; H 8.30; 8.30

$C_{10}H_{21}O_5P$. Calculated %: C 47.61; H 8.32

Dipropyl 2-(2-Ethoxyethoxy)vinylphosphonate $C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OC_3H_7\text{-}n)_2$. 2-(2-Ethoxyethoxy)vinylphosphonic dichloride (10 g) was added to a mixture of 6.8 g of pyridine, 5.2 g of absolute propyl alcohol, and 100 ml of dry benzene. The product, amounting to 9.7 g (80%), had b.p. 140° (2 mm); n_D^{20} 1.4510; d_4^{20} 1.0470.

Found %: C 51.34; 51.75; H 9.00; 9.25

$C_{12}H_{25}O_5P$. Calculated %: C 51.42; H 8.92

Diisopropyl 2-(2-Ethoxyethoxy)vinylphosphonate $C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OC_3H_7\text{-}i)_2$. 2-(2-Ethoxyethoxy)vinylphosphonic dichloride (15 g) was added to a mixture of 8 g of isopropyl alcohol and 11 g of pyridine. Vacuum fractionation yielded 13 g (72%) of product, b.p. 123° (2 mm); n_D^{20} 1.4452; d_4^{20} 1.0341.

Found %: C 51.39; 51.76; H 9.10; 9.02

$C_{12}H_{25}O_5P$. Calculated %: C 51.42; H 8.92

Diisobutyl 2-(2-Ethoxyethoxy)vinylphosphonate $C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OC_4H_9\text{-}i)_2$. 2-(2-Ethoxyethoxy)vinylphosphonic dichloride (11.65 g) was added to a mixture of 7.5 g of absolute isobutyl alcohol and 8 g of pyridine. The product, amounting to 12.6 g (82%), had b.p. 143° (2 mm); n_D^{20} 1.4492; d_4^{20} 1.0159.

Found %: P 9.89; 9.97

$C_{14}H_{29}O_5P$. Calculated %: P 10.06

Diallyl 2-(2-Ethoxyethoxy)vinylphosphonate $C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OC_3H_5)_2$. 2-(2-Ethoxyethoxy)vinylphosphonic dichloride (10 g) was added to a cooled mixture of 5 g of absolute allyl alcohol, 7 g of pyridine, and 70 ml of dry benzene. Fractional distillation yielded 9 g (77%) of product, b.p. 138.5° (2 mm); n_D^{20} 1.4702; d_4^{20} 1.0854.

Found %: C 52.10; 51.83; H 7.86; 8.04

$C_{12}H_{21}O_5P$. Calculated %: C 52.17; H 7.60

Diheptyl 2-(2-Ethoxyethoxy)vinylphosphonate $C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OC_7H_{15}\text{-}n)_2$. 2-(2-Ethoxyethoxy)vinylphosphonic dichloride (11.65 g) was added to a mixture of 11.7 g of absolute heptyl alcohol, 8 g of pyridine, and 110 ml of benzene. The product (17 g) had b.p. 200° (1 mm); n_D^{20} 1.4546; d_4^{20} 0.9745.

Found %: C 61.64; 61.79; H 10.52; 10.53; P 7.86; 7.67;

$C_{20}H_{41}O_5P$. Calculated %: C 61.22; H 10.45; P 7.90

Bis(2-methoxyethyl) 2-(2-Ethoxyethoxy)vinylphosphonate $C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OCH-CH_2-$ $-OCH_3)_2$. Reaction between 11.65 g of 2-(2-ethoxyethoxy)vinylphosphonic dichloride, 7 g of 2-methoxyethanol, and 8 g of pyridine in 100 ml of benzene yielded, after vacuum fractionation, 13.2 g (84%) of product, b.p. 163° (1 mm); n_D^{20} 1.4602; d_4^{20} 1.1279.

Found %: P 9.57; 9.67

$C_{12}H_{25}O_7P$. Calculated %: P 9.93

Bis(2-ethoxyethyl) 2-(2-Ethoxyethoxy)vinylphosphonate $C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OCH_2-CH_2-$ $-OC_2H_5)_2$. Reaction between 8 g of 2-ethoxyethanol, 7 g of pyridine, and 10 g of 2-(2-ethoxyethoxy)vinylphosphonic dichloride yielded 12 g (86%) of product, b.p. 180° (1 mm); n_D^{20} 1.4565; d_4^{20} 1.0917.

Found %: C 49.55; 49.42; H 8.68; 8.90

$C_{14}H_{29}O_7P$. Calculated %: C 49.41; H 8.52

2-(2-Butoxyethoxy)vinylphosphonic Esters

Dimethyl 2-(2-Butoxyethoxy)vinylphosphonate $n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO(OCH_3)_2$. Reaction between 2.5 g of absolute methanol, 6.2 g of pyridine, and 10 g of 2-(2-butoxyethoxy)vinylphosphonic dichloride yielded 7.4 g (77%) of product, b.p. 132° (1 mm); n_D^{20} 1.4565; d_4^{20} 1.1100.

Found %: C 47.41; 47.61; H 8.41; 8.61

$C_{10}H_{21}O_5P$. Calculated %: C 47.61; H 8.33

Diethyl 2-(2-Butoxyethoxy)vinylphosphonate $n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO(OC_2H_5)_2$. 2-(2-Butoxyethoxy)vinylphosphonic dichloride (13.5 g) was added with stirring and cooling to a mixture of 4.8 g of absolute ethanol, 7 g of pyridine, and 80 ml of dry benzene. The product, amounting to 11.5 g (79%), had b.p. 155° (2 mm); n_D^{20} 1.4519; d_4^{20} 1.0615.

Found %: C 51.86; 51.82; H 9.12; 9.23

$C_{12}H_{25}O_5P$. Calculated %: C 51.42; H 8.90

Dipropyl 2-(2-Butoxyethoxy)vinylphosphonate $n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO(OC_3H_7\text{-}n)_2$. 2-(2-Butoxyethoxy)vinylphosphonic dichloride (10 g) was added to a cooled mixture of 4.6 g of absolute propyl alcohol, 6.2 g of pyridine, and 100 ml of dry benzene. The product, amounting to 9.5 g (83%), had b.p. 163° (2 mm); n_D^{20} 1.4529; d_4^{20} 1.0199.

Found %: C 54.48; 54.68; H 9.72; 9.74; P 10.58; 10,35

$C_{14}H_{29}O_5P$. Calculated %: C 54.54; H 9.41; P 10.06

Dibutyl 2-(2-Butoxyethoxy)vinylphosphonate $n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO(OC_4H_9\text{-}n)_2$. 2-(2-Butoxyethoxy)vinylphosphonic dichloride (12 g) was added to a mixture of 6.7 g of absolute butyl alcohol and 8 g of pyridine. The product, amounting to 13.5 g (88%), had b.p. 180° (2 mm); n_D^{20} 1.4532; d_4^{20} 1.0008.

Found %: C 56.90; 57.14; H 10.68; 10.04; P 8.86; 9.17

$C_{16}H_{33}O_5P$. Calculated %: C 57.14 H 9.82 P 9.22

Diisobutyl 2-(2-Butoxyethoxy)vinylphosphonate $n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO(OC_4H_9\text{-}i)_2$. 2-(2-Butoxyethoxy)vinylphosphonic dichloride (13.5 g) was added to a mixture of 7.5 g of absolute isobutyl alcohol, 8 g of pyridine, and 75 ml of benzene. The product, amounting to 14.2 g (83%), had b.p. 172° (2 mm); n_D^{20} 1.4512; d_4^{20} 1.0002.

Found %: C 57.33; 57.28; H 10.21; 10.20; P 8.71; 8.90

$C_{16}H_{33}O_5P$. Calculated %: C 57.14 H 9.82 P 9.22

Diallyl 2-(2-Butoxyethoxy)vinylphosphonate $n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO(OC_3H_5)_2$. 2-(2-Butoxyethoxy)vinylphosphonic dichloride (10 g) was added to a cooled mixture of 4.5 g of absolute allyl alcohol, 6.5 g of pyridine, and 120 ml of dry benzene. The product, amounting to 8.2 g (72%), had b.p. 152° (1 mm); n_D^{20} 1.4680; d_4^{20} 1.0530.

Found %: C 55.32; 55.48; H 8.39; 8.35; P 9.79; 9.88

$C_{14}H_{25}O_5P$. Calculated %: C 55.26; H 8.22; P 10.19

Dihexyl 2-(2-Butoxyethoxy)vinylphosphonate $n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO(OC_6H_{13}\text{-}n)_2$. 2-(2-Butoxyethoxy)vinylphosphonic dichloride (10 g) was added to a mixture of 8 g of absolute hexyl alcohol, 7.8 g of pyridine, and 100 ml of benzene. The product, amounting to 12.7 g (85%), had b.p. 202° (2 mm); n_D^{20} 1.4550; d_4^{20} 0.9734.

Found %: C 60.92; 61.02; H 10.75; 10.82

$C_{20}H_{41}O_5P$. Calculated %: C 61.22; H 10.45

Diheptyl 2-(2-Butoxyethoxy)vinylphosphonate $n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO(OC_7H_{15}\text{-}n)_2$. 2-(2-Butoxyethoxy)vinylphosphonic dichloride (13.1 g) was added to a mixture of 11.8 g of absolute heptyl alcohol, 8 g of pyridine, and 85 ml of dry benzene. The product, amounting to 18.6 g (89%), had b.p. 207° (1 mm); n_D^{20} 1.4553; d_4^{20} 0.9644.

Found %: C 63.10; 63.10; H 10.75; 10.71; P 7.53; 7.55

$C_{22}H_{45}O_5P$. Calculated %: C 62.85; H 10.70; P 7.32

Bis(2-ethoxyethyl) 2-(2-Butoxyethoxy)vinylphosphonate $n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO(OCH_2-CH_2-O-C_2H_5)_2$. 2-(2-Butoxyethoxy)vinylphosphonic dichloride (13.5 g) was added to a mixture of 9 g of 2-ethoxyethanol, 8 g of pyridine, and 100 ml of dry benzene. The product, amounting to 16.5 g (87%), had b.p. 193° (2 mm); n_D^{20} 1.4561; d_4^{20} 1.0643.

Found %: C 52.00; 51.77; H 9.29; 9.32; P 8.77; 8.71

$C_{16}H_{33}O_7P$. Calculated %: C 52.18; H 8.96; P 8.42

SUMMARY

Twenty-nine diesters of 2-(2-methoxyethoxy)-, 2-(2-ethoxyethoxy)-, and 2-(2-butoxyethoxy)-vinylphosphonic acids have been prepared and characterized.

LITERATURE CITED

[1] M. Milobendzki, A. Sachnowski, Chem. Polski, 15, 34 (1917).

Received June 11, 1954

Institute of Heteroorganic Compounds
of the USSR Academy of Sciences

DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 12. BISDIALKYLAMIDES OF 2-(2-ALKOXYETHOXY)VINYLPHOSPHONIC ACIDS

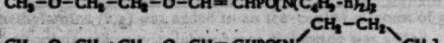
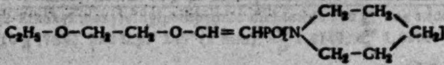
K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov

When dialkylamines react with 2-(2-alkoxyethoxy)vinylphosphonic dichlorides, bisdialkylamides of 2-(2-alkoxyethoxy)vinylphosphonic acids are formed in almost quantitative yield.

We have prepared and characterized the bisdimethylamides, bisdiethylamides, bisdipropylamides, bisdibutylamides, and dipiperidides of 2-(2-methoxyethoxy)-, 2-(2-ethoxyethoxy)-, and 2-(2-butoxyethoxy)vinylphosphonic acids. These substances are liquids which can be readily distilled under reduced pressure. They are soluble in all organic solvents, and some of them are soluble also in water. All bisdialkylamides of 2-(2-alkoxyethoxy)vinylphosphonic acids are stable to storage.

Their constants are given in Table 1.

TABLE 1

Formula	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	Yield (%)
$CH_3-O-CH_2-CH_2-O-CH=CHPO[N(CH_3)_2]_2$	144 (2)	1.4808	1.0879	56
$CH_3-O-CH_2-CH_2-O-CH=CHPO[N(C_2H_5)_2]_2$	153 (2)	1.4765	1.0191	59
$CH_3-O-CH_2-CH_2-O-CH=CHPO[N(C_3H_7\text{-n})_2]_2$	160 (1)	1.4733	0.9932	65
$CH_3-O-CH_2-CH_2-O-CH=CHPO[N(C_4H_9\text{-n})_2]_2$	183 (1)	1.4710	0.9741	75
	187 (1)	1.5101	1.1026	84
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO[N(CH_3)_2]_2$	143 (2)	1.4770	1.0545	72
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO[N(C_2H_5)_2]_2$	146 (1)	1.4749	1.0108	78
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO[N(C_3H_7\text{-n})_2]_2$	163 (2)	1.4721	0.9822	83
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO[N(C_4H_9\text{-n})_2]_2$	180 (1)	1.4705	0.9579	93
	185 (2)	1.5062	1.0851	96
$n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO[N(CH_3)_2]_2$	175 (2)	1.4758	1.0274	71
$n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO[N(C_2H_5)_2]_2$	179 (2)	1.4730	0.9948	87

EXPERIMENTAL

Bisdimethylamide of 2-(2-Methoxyethoxy)vinylphosphonic Acid $CH_3-O-CH_2-CH_2-O-CH=CHPO[N(CH_3)_2]_2$. A solution of 13 g of dimethylamine in 100 ml of petroleum ether was poured into a three-necked flask, fitted with stirrer and reflux condenser and cooled with ice and salt. The solution was stirred while 15.8 g of 2-(2-methoxyethoxy)vinylphosphonic dichloride was added. On the next day, after the mixture had been heated for two hours at 30° in a water bath, dimethylamine hydrochloride was filtered off, and the filtrate was treated with 10% sodium carbonate solution and dried over potassium carbonate. Vacuum fractionation yielded 9.5 g (56%) of a substance having b.p. 144° (2 mm); n_D^{21} 1.4808; d_4^{20} 1.0879.

Found %: P 12.97; 13.04

$C_9H_{21}O_3PN_2$. Calculated %: P 13.26

The other bisdialkylamides were prepared under conditions similar to those described above.

Bisdiethylamide of 2-(2-Methoxyethoxy)vinylphosphonic Acid $CH_3-O-CH_2-CH_2-O-CH=CHPO[N(C_2H_5)_2]_2$. 2-(2-Methoxyethoxy)vinylphosphonic dichloride (10.85 g) was added to a solution of 15 g of diethylamine in 120 ml of a mixture of petroleum ether and benzene. The product, amounting to 8.6 g, had b.p. 153° (2 mm); n_D^{20} 1.4765; d_4^{20} 1.0191.

Found %: P 10.60; 10.52

$C_{13}H_{29}O_3PN_2$. Calculated %: P 10.61

Bisdipropylamide of 2-(2-Methoxyethoxy)vinylphosphonic Acid $CH_3-O-CH_2-CH_2-O-CH=$ $=CHPO[N(C_3H_7\text{-}n)_2]_2$. Reaction of 8.13 g of 2-(2-methoxyethoxy)vinylphosphonic dichloride with 16 g of dipropylamine yielded 8.5 g (65%) of a substance having b.p. 160° (1 mm); n_D^{20} 1.4733; d_4^{20} 0.9932.

Found %: P 8.81; 8.98

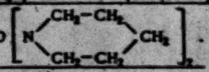
$C_{17}H_{37}O_3PN_2$. Calculated %: P 8.90

Bisdibutylamide of 2-(2-Methoxyethoxy)vinylphosphonic Acid $CH_3-O-CH_2-CH_2-O-CH=CHPO[N(C_4H_9\text{-}n)_2]_2$. 2-(2-Methoxyethoxy)vinylphosphonic dichloride (10.85 g) was added to 30 g of dibutylamine. The product, amounting to 15 g (75%), had b.p. 183° (1 mm); n_D^{20} 1.4710; d_4^{20} 0.9741.

Found %: N 6.64; 6.65

$C_{21}H_{45}O_3N_2P$. Calculated %: N 6.93

Dipiperidide of 2-(2-Methoxyethoxy)vinylphosphonic Acid $CH_3-O-CH_2-CH_2-O-CH=$ $=CHPO$



. Piperidine (20 g) was added to 10.85 g of 2-(2-methoxyethoxy)vinylphosphonic dichloride. The product, amounting to 14.4 g (84%), had b.p. 187° (1 mm); n_D^{20} 1.5101; d_4^{20} 1.1026.

Found %: P 9.47; 9.53

$C_{15}H_{27}O_3PN_2$. Calculated %: P 9.80

Bisdimethylamide of 2-(2-Ethoxyethoxy)vinylphosphonic Acid $C_2H_5-O-CH_2-CH_2-O-CH=CHPO[N(CH_3)_2]_2$. Dimethylamine (9 g) was added to an ice-cooled mixture of petroleum ether and benzene. To this mixture, 10.65 g of 2-(2-ethoxyethoxy)vinylphosphonic dichloride was added. The product, amounting to 8.2 g (72%), had b.p. 143° (2 mm); n_D^{20} 1.4770; d_4^{20} 1.0545.

Found %: N 11.20; 10.59

$C_{10}H_{23}O_3PN_2$. Calculated %: N 11.20

Bisdiethylamide of 2-(2-Ethoxyethoxy)vinylphosphonic Acid $C_2H_5-O-CH_2-CH_2-O-CH=CHPO[N(C_2H_5)_2]_2$. 2-(2-Ethoxyethoxy)vinylphosphonic dichloride (10 g) was added to 12.5 g of diethylamine. The product, amounting to 10 g (78%), had b.p. 146° (2 mm); n_D^{20} 1.4749; d_4^{20} 1.0108.

Found %: N 8.96; 9.13

$C_{14}H_{31}O_3PN_2$. Calculated %: N 9.15

Bisdipropylamide of 2-(2-Ethoxyethoxy)vinylphosphonic Acid $C_2H_5-O-CH_2-CH_2-O-CH=CHPO[N(C_3H_7\text{-}n)_2]_2$. 2-(2-Ethoxyethoxy)vinylphosphonic dichloride (10 g) was added to 18 g of dipropylamine. The product, amounting to 12.8 g (83%), had b.p. 163° (2 mm); n_D^{20} 1.4721; d_4^{20} 0.9822.

Found %: N 7.61; 7.65

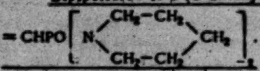
$C_{18}H_{39}O_3PN_2$. Calculated %: N 7.73

Bisdibutylamide of 2-(2-Ethoxyethoxy)vinylphosphonic Acid $C_2H_5-O-CH_2-CH_2-O-CH=CHPO[N(C_4H_9\text{-}n)_2]_2$. 2-(2-Ethoxyethoxy)vinylphosphonic dichloride (10 g) was added to 23 g of dibutylamine. The product, amounting to 16.5 g (93%), had b.p. 180° (1 mm); n_D^{20} 1.4705; d_4^{20} 0.9579.

Found %: N 6.86; 6.63

$C_{22}H_{47}O_3PN_2$. Calculated %: N 6.69

Dipiperidide of 2-(2-Ethoxyethoxy)vinylphosphonic Acid $C_2H_5-O-CH_2-CH_2-O-CH=$



. Reaction between 10 g of 2-(2-ethoxyethoxy)vinylphosphonic dichloride and 15 g of piperidine yielded 13.5 g (96%) of a substance having b.p. 185° (1 mm); n_D^{20} 1.5062; d_4^{20} 1.0851.

Found %: N 8.58; 8.77

$C_{16}H_{31}O_3PN_2$. Calculated %: N 8.48

Bisdimethylamide of 2-(2-Butoxyethoxy)vinylphosphonic Acid $n-C_4H_9-O-CH_2-CH_2-O-CH=CHPO[N(CH_3)_2]_2$. Dimethylamine (9 g) was added to an ice-cooled mixture of petroleum ether and benzene, and then, gradually and with stirring, 12 g of 2-(2-butoxyethoxy)vinylphosphonic dichloride was added. The product, amounting to 9 g (71%), had b.p. 175° (2 mm); n_D^{20} 1.4758; d_4^{20} 1.0274.

Found %: P 10.82; 11.02

$C_{12}H_{27}O_3PN_2$. Calculated %: P 11.15

Bisdiethylamide of 2-(2-Butoxyethoxy)vinylphosphonic Acid $n-C_4H_9-O-CH_2-CH_2-O-CH=CHPO[N(C_2H_5)_2]_2$. Reaction of 13.5 g of 2-(2-butoxyethoxy)vinylphosphonic dichloride with 15 g of diethylamine yielded 15 g (87%) of a substance having b.p. 179° (2 mm); n_D^{20} 1.4730; d_4^{20} 0.9948.

Found %: P 9.20; 9.21

$C_{16}H_{35}O_3PN_2$. Calculated %: P 9.28

SUMMARY

Twelve bisdialkylamides of 2-(2-alkoxyethoxy)vinylphosphonic acids have been synthesized and characterized.

Received June 11, 1954

Institute of Heteroorganic Compounds
of the USSR Academy of Sciences

SYNTHESIS OF ALKOXYBROMOTITANIUMS AND ALKOXYCHLOROPOLYTITANOXANES

A. N. Nesmeyanov, E. M. Brainina, and R. Kh. Freidlina

Several methods have been proposed in recent years for the synthesis of alkoxychlorotitaniums, and, as a result, compounds of this type containing one, two, and three chlorine atoms in their molecules have become readily accessible [1-3, 9, 11, 13-16]. The only alkoxybromotitaniums known are dialkoxydibromotitaniums obtained in the form of double compounds with alcohols: $(RO)_2TiBr_2 \cdot ROH$. These compounds were prepared by two of the present authors in collaboration with Nogina [1] by the action of bromine on alkyl orthotitanates.

A few papers and patents have been devoted to the preparation and study of organopolytitanoxanes [4-8, 12, 17]. It was found that polymeric compounds are formed in the thermal decomposition of alkyl orthotitanates [4-6, 12]. In the thermal decomposition of butyl orthotitanate, the products, apart from titanium-containing polymer, include butyl alcohol and butyraldehyde according to one investigation [6], and butyl alcohol and butene, according to others [5, 12]. The thermal decomposition of alkyl orthotitanates cannot be regarded as a convenient method of synthesizing polytitanoxanes, since the reaction requires long heating at a high temperature, and is not controllable [5].

Another method for the preparation of compounds containing the polytitanoxane chain is the action of water on alkyl orthotitanates [6-8, 17]. It is reported [7, 17] that linear polymers are formed by the action of water on butyl orthotitanate so long as the molar ratio of the water and ester taken for reaction is not greater than unity. In the same papers it is stated that with such proportions of water and ester the polymers formed have a medium degree of polymerization (estimated from the titanium content of the polymer) corresponding to that calculated from the equation:

$$n(RO)_4Ti + (n-1)\,H_2O \rightarrow (RO)_{2n+2}Ti_nO_{n-1} + 2\,(n-1)\,ROH.$$

According to our results [8], by reaction of one molecular proportion of water with two molecular proportions of ethyl orthotitanate, not hexaethoxydititanoxane $(C_2H_5O)_6Ti_2O$, (in accordance with the equation), but octaethoxytrititanoxane $(C_2H_5O)_8Ti_3O_2$, is formed.

The investigation of polyalkoxypolytitanoxanes is rendered difficult by the fact that these substances are usually highly viscous liquids, which decompose when distilled under reduced pressure (2-3 mm). The purification of these compounds by other methods is rendered difficult by the extreme readiness with which they undergo hydrolysis. Molecular weight determinations on these substances do not usually yield unequivocal results, since polyalkoxypolytitanoxanes are associated in solution and the degree of association depends on the concentration. It is characteristic of these compounds that each repeating unit of the chain, which contains one titanium atom, is multifunctional, a fact that makes it difficult to establish the structures of these compounds.

At the present stage of development in this field, special interest is presented by polyalkoxypolytitanoxanes containing only a few titanium atoms in the polytitanoxane chain, since these compounds can be more readily isolated and identified. Up to the present, apart from octaethoxytrititanoxane, described by us [8], hexabutoxydititanoxane $(C_4H_9O)_6Ti_2O$ [12, 7] and hexaallyloxydititanoxane $(C_3H_5O)_6Ti_2O$ [6] have been described. Hexabutoxydititanoxane was prepared both by the thermal decomposition of butyl orthotitanate and by the action of water on this ester [12]. This compound was not purified in any way; its composition was established merely by analysis for titanium.

In the thermal decomposition of allyl orthotitanate, a residue was obtained which roughly corresponded in analysis to hexaallyloxydititanoxane; the experimentally determined molecular weight differed greatly from the calculated value [6].

No organopolytitanoxanes containing halogen have been described.

Octaethoxytrititanoxane $(C_2H_5O)_8Ti_3O_2$, which we prepared by the hydrolysis of ethyl orthotitanate, is a crystalline substance and can be purified by recrystallization from alcohol or benzene; its composition was established by analysis for carbon, hydrogen, and titanium [8]. The determination of the molecular weight of this compound in fairly dilute benzene solution by the cryoscopic method gave a value close to the calculated value [8].

In the present paper we describe the conversion of octaethoxytrititanoxane into other octaalkoxytrititanoxanes by transesterification:

$$(C_2H_5O)_8Ti_3O_2 + 8\,ROH \rightarrow (RO)_8Ti_3O_2 + 8C_2H_5OH,$$

in which $R = n\text{-}C_4H_9$ and $n\text{-}C_6H_{13}$.

The resulting octabutoxy- and octahexyloxy-trititanoxanes were found to be viscous liquids. When attempts were made to distil them at 2-5 mm, butyl and hexyl orthotitanates were obtained, respectively. It was further shown that equimolecular amounts of octaethoxytrititanoxane and acetyl chloride react together with formation of a chloroheptaethoxytrititanoxane and ethyl acetate, in accordance with the equation (see also [14]):

$$(C_2H_5O)_8Ti_3O_2 + CH_3COCl \rightarrow (C_2H_5O)_7Ti_3O_2Cl + CH_3CO_2C_2H_5.$$

When octaalkoxytrititanoxanes reacted with two molecular proportions of acetyl chloride, hexaalkoxydichlorotrititanoxanes and alkyl acetates were obtained, in accordance with the equation:

$$(RO)_8Ti_3O_2 + 2\,CH_3COCl \rightarrow (RO)_6Ti_3O_2Cl_2 + 2CH_3CO_2R,$$

in which $R = C_2H_5$, $n\text{-}C_4H_9$, $n\text{-}C_6H_{13}$.

Of all of the chlorotrititanoxanes prepared, only compounds containing ethoxy groups were found to be solids, the remainder being viscous liquids. The positions of the chlorines in these compounds were not investigated. When hexaalkoxydichlorotitanoxanes were vacuum-distilled, the corresponding trialkoxychlorotitaniums were obtained.

We have studied also the reaction of disproportionation in reverse for the purpose of the synthesis of alkoxybromotitaniums. In the reaction of ethyl orthotitanate with titanium tetrabromide at room temperature we obtained, depending on the proportion of reactants, different bromoethoxytitaniums in accordance with the equations:

$$(RO)_4Ti + TiBr_4 \rightarrow 2(RO)_2TiBr_2$$

$$(RO)_4Ti + 3TiBr_4 \text{ — } 4ROTiBr_3.$$

This reaction, like that between an alkyl orthotitanate and titanium tetrachloride [2, 3], can be carried out in presence of the calculated amount of piperidine, when crystalline double compounds of formula:

$$(RO)_nTiBr_{4-n}\ C_5H_{10}NH,$$

are formed between the bromoethoxytitanium and piperidine (n = 1 and 2).

These double compounds are readily purified by recrystallization.

EXPERIMENTAL

All experiments were carried out under conditions that precluded access of atmospheric moisture; all substances were carefully dried.

Octaethoxytrititanoxane * $(C_2H_5O)_8Ti_3O_2$. A solution of 1.31 g (0.073 mole) of water in 10 ml of absolute alcohol was added gradually with vigorous stirring to a solution of 33.7 g (0.147 mole) of ethyl orthotitanate in 15 ml of absolute alcohol. The reaction mixture was then heated to the boil, when most of the precipitate that had formed was dissolved. The hot solution was filtered from the small amount of insoluble residue. The filtrate was

---

* We have already given a brief description of the preparation of this compound and some of its properties [8].

cooled and yielded 14.6 g of precipitate, which corresponds to a 75% yield, on the basis of the amount of water taken for reaction. The analysis of the non-crystallized product was closely in accord with that calculated for octaethoxytrititanoxane. The product was recrystallized from the least possible amount (7 ml) of alcohol and again analyzed.

Found %: C 35.95; 35.95; H 7.57; 7.56; Ti 26.45; 26.54
$(C_2H_5O)_8Ti_3O_2$. Calculated %: C 35.82; H 7.52; Ti 26.81

The substance melts in a sealed capillary over a wide range of temperature (~ 78-85°). Careful evaporation of the mother liquor gave still a little more octaethoxytrititanoxane; under these conditions, therefore, no polymers differing in degree of polymerization are formed.

Octabutoxytrititanoxane $(n\text{-}C_4H_9O)_8Ti_3O_2$. A solution of 10.7 g of recrystallized octaethoxytrititanoxane in 20 ml of butyl alcohol was heated for two hours. The alcohols present were then distilled off. More butyl alcohol was added, and the operation was repeated, when it was found that pure butyl alcohol came over. The butyl alcohol was distilled off under reduced pressure. The residual viscous liquid was dissolved in petroleum ether, and the solution was filtered. Attempts to crystallize the substance from this solution were not successful, and the solvent was therefore distilled off, the residue being carefully freed from volatile substances by heating at 90° under a residual pressure of 3 mm for 40 minutes. Octabutoxytrititanoxane is a light-yellow viscous liquid. It is hygroscopic, and it readily undergoes hydrolysis.

Found %: C 50.63; 50.80; 50.71; H 9.74; 9.70; 9.60; Ti 19.13; 19.04; 18.91
$(C_4H_9O_8)Ti_3O_2$. Calculated %: C 50.51 H 9.70; Ti 18.90

When octabutoxytrititanoxane (19 g) was heated in an oil bath at 200-220°, butyl orthotitanate distilled off (the temperature in the vapor was 149-150° at a residual pressure of 2-3 mm), the amount collected being 5.2 g. Solid polymer remained behind in the distilling flask. When redistilled, the butyl orthotitanate boiled at 167-167.5° (5 mm).

Found %: C 55.86; 55.94; H 10.69; 10.82; Ti 13.98; 14.19
$(C_4H_9O)_4Ti$. Calculated %: C 56.45; H 10.66; Ti 14.08

For $(C_4H_9O)_4Ti$ the literature [9] gives b.p 160-162° (2 mm).

Octahexyloxytrititanoxane $(n\text{-}C_6H_{13}O)_8Ti_3O_2$. The procedure was the same as in the preceding experiment. Reaction between 4.3 g of octaethoxytrititanoxane and 55 ml of hexyl alcohol gave a quantitative yield of liquid octahexyloxytrititanoxane.

Found %: C 58.48; 58.76; H 10.54; 10.59; Ti 14.60; 14.36
$(C_6H_{13}O)_8Ti_3O_2$. Calculated %: C 58.51; H 10.65; Ti 14.60

When 21.1 g of octahexyloxytrititanoxane was heated in a water bath at 250-260°, hexyl orthotitanate distilled off (the temperature in the vapor was 208-205° at a residual pressure of 2.5 mm), the amount collected being 10.7 g. After redistillation the hexyl orthotitanate boiled at 199° (2 mm); it had n_D^{20} 1.4840.

Found %: C 63.61; 64.07; H 11.62; 11.75; Ti 10.29; 10.30
$(C_6H_{13}O)_4Ti$. Calculated %: C 63.66; H 11.60; Ti 10.59

For $(n\text{-}C_6H_{13}O)_4Ti$ the literature [10] gives b.p. 201-204° (2 mm), n_D^{20} 1.4830.

Chloroheptaethoxytrititanoxane $(C_2H_5O)_7Ti_3O_2Cl$. A solution of 0.78 g (0.01 mole) of acetyl chloride in 3 ml of petroleum ether was added to a cooled solution of 5.36 g (0.01 mole) of octaethoxytrititanoxane in 5 ml of petroleum ether. The reaction mixture was heated for two hours at 70-75°, cooled, and filtered from suspended matter. Solvent and ethyl acetate was distilled from the filtrate. The solid product was very readily soluble in petroleum ether. Attempts to recrystallize it from this solvent with cooling to −70° were not successful. The product was freed from volatile impurities by heating it for two hours at 50° at a residual pressure of 2 mm. When heated in a sealed capillary, the substance melted over a wide temperature range.

Found %: C 32.24; 32.24; H 6.83; 6.64; Ti 26.79; 26.73
$(C_2H_5O)_7Ti_3O_2Cl$. Calculated %: C 31.91; H 6.68; Ti 27.30

Dichlorohexaethoxytrititanoxane $(C_2H_5O)_6Ti_3O_2Cl_2$. The procedure was as in the preceding experiment. Treatment of a solution of 4.8 g (0.0089 mole) of octaethoxytrititanoxane in 5 ml of petroleum ether with a solution of 1.4 g (0.0178 mole) of acetyl chloride in 3 ml of petroleum ether yielded 3.7 g (which corresponds to a quantitative yield) of solid dichlorohexaethoxytrititanoxane.

Found %: C 28.20; 27.96; H 6.10; 6.09; Ti 27.43; 27.61
$(C_2H_5O)_6Ti_3O_2Cl_2$. Calculated %: C 27.87; H 5.83; Ti 27.81

The product was recrystallized from petroleum ether and filtered off through a funnel cooled with a mixture of acetone and dry ice. The residue on the filter was dissolved in a new portion of petroleum ether, and solvent was then removed completely under reduced pressure.

Found %: Cl 14.19; 14.20
Calculated %: Cl 13.74

Hexabutoxydichlorotrititanoxane $(n\text{-}C_4H_9O)_6Ti_3O_2Cl_2$. The procedure was as in the preceding experiments. Treatment of a solution of 11.45 g (0.015 mole) of octabutoxytrititanoxane in 15 ml of petroleum ether with a solution of 2.36 g (0.030) mole) of acetyl chloride in 5 ml of benzene gave 9.5 g (92%) of hexabutoxydichlorotrititanoxane, in the form of a viscous liquid.

Found %: C 41.98; 41.86; H 7.91; 7.93; Cl 10.26; 10.59; Ti 20.70; 20.81
$(C_4H_9O)_6Ti_3O_2Cl_2$. Calculated %: C 42.04; H 7.94 Cl 10.35; Ti 20.98

When 4.33 g of the product was vacuum-distilled, some liquid (1.83 g) came over at 145-146° (1 mm). Solid polymer remained behind in the distilling flask. Redistillation of the distillate yielded tributoxychlorotitanium, b.p. 156.5° (2.5 mm); n_D^{20} 1.5192.

Found %: C 47.51; 47.54; H 8.96; 9.00; Ti 15.55; 16.09
$(C_4H_9O)_3TiCl$. Calculated %: C 47.61; H 8.99 Ti 15.82

For tributoxychlorotitanium the literature [11] gives b.p. 154-155° (2 mm); n_D^{20} 1.5169.

Dichlorohexahexyloxytrititanoxane $(n\text{-}C_6H_{13}O)_6Ti_3O_2Cl_2$. The procedure was as in the preceding experiments. Treatment of a solution of 14.82 g (0.015 mole) of octahexyloxytrititanoxane in 10 ml of petroleum ether with a solution of 2.36 g (0.030 mole) of acetyl chloride in 3 ml of petroleum ether yielded liquid dichlorohexahexyloxytrititanoxane.

Found %: C 50.54; 50.39; H 9.18; 9.21; Ti 16.91; 16.99
$(C_6H_{13}O)_6Ti_3O_2Cl_2$. Calculated %: C 50.63; H 9.21; Ti 16.84

When 10 g of the product was distilled, a substance boiling at 178° (1 mm) came over. Solid polymer (2 g) remained behind in the flask. Redistillation of the distillate yielded chlorotrihexyloxytitanium, b.p. 198-201° (2 mm); n_D^{20} 1.5060.

Found %: C 55.16; 55.20; H 10.14; 10.10; Ti 12.02; 11.80
$(C_6H_{13}O)_3TiCl$. Calculated %: C 55.88; H 10.16; Ti 12.38

For chlorotrihexyloxytitanium the literature [11] gives b.p. 182-182.5° (1 mm); n_D^{20} 1.5050.

Dibromodiethoxytitanium $(C_2H_5O)_2TiBr_2$. A solution of 1.84 g (0.005 mole) of freshly distilled titanium tetrabromide in 5 ml of benzene was added to a solution of 1.14 g (0.005 mole) of ethyl orthotitanate in 6 ml of a mixture of equal volumes of benzene and petroleum ether. The reaction mixture was cooled at −10 to −15° for a long time, and a precipitate finally formed (2.29 g, i.e. 79%). It was recrystallized from benzene and dried in a current of dry air. When heated in a sealed capillary, the substance melted with decomposition over the range 47-50° with formation of a red liquid.

Found %: C 16.36; 16.21; H 3.74; 3.62; Ti 16.38; 16.44
$(C_2H_5O)_2TiBr_2$. Calculated %: C 16.12; H 3.38 Ti 16.09

Tribromoethoxytitanium $C_2H_5OTiBr_3$. The procedure was as in the preceding experiment. A solution of 11.02 g (0.03 mole) of titanium tetrabromide in 5 ml of benzene was treated with a solution of 2.28 g (0.01 mole) of ethyl orthotitanate in 3 ml of petroleum ether, the resulting mixture being cooled for one day. The precipitate that then formed amounted to 5.8 g (45%). It was found possible to obtain a little more of this compound by careful evaporation of the mother liquor. The substance was recrystallized from a mixture of benzene and petroleum ether.

Found %: C 7.96; 7.99; H 1.87; 1.73; Ti 14.41; 14.20

$(C_2H_5O)TiBr_3$. Calculated %: C 7.23; H 1.51; Ti 14.43

When heated in a sealed capillary, the substance melted over an extended range.

Double Compound formed by Dibromodiethoxytitanium with Piperidine $(C_2H_5O)_2TiBr_2C_5H_{10}NH$. A solution of 1.70 g (0.02 mole) of piperidine in 3 ml of benzene was added to a cooled solution of 2.28 g (0.01 mole) of ethyl orthotitanate in 3 ml of petroleum ether. A solution of 3.67 g (0.01 mole) of titanium tetrabromide in 5 ml of benzene was then added dropwise to the resulting mixture, when a light-yellow precipitate formed. The mixture was set aside overnight, and the precipitate was then filtered off, washed with petroleum ether, and dried (6.13 g, i.e. 80%). It was recrystallized from benzene.

Found %: C 29.06; 28.96; H 5.72; 5.52; Ti 12.31; 12.27;
N 3.48; 3.44

$(C_2H_5O)_2TiBr_2C_5H_{11}N$. Calculated %: C 28.20; H 5.52; Ti 12.51; N 3.65

Double Compound formed by Bromotriethoxytitanium with Piperidine $(C_2H_5O)_3TiBrC_5H_{10}NH$. The procedure was as in the preceding experiment. Reaction of 6.48 g (0.03 mole) of ethyl orthotitanate, 3.40 g (0.04 mole) of piperidine, and 3.67 g (0.01 mole) of titanium tetrabromide in the least possible volume of a mixture of benzene and petroleum ether yielded 10.48 g (75%) of the double compound. The substance was recrystallized from a mixture of benzene and petroleum ether.

Found %: C 37.89; 37.85; H 7.38; 7.40; Br 22.94; 23.85;
Ti 13.70; 13.75; N 4.02; 3.87

$(C_2H_5O)_3TiBrC_5H_{10}NH$. Calculated %: C 37.93; H 7.52; Br 23.06; Ti 13.76; N 4.02

SUMMARY

1. By the transesterification of octaethoxytrititanoxane, octabutoxy- and octahexyloxy-trititanoxanes $(n\text{-}C_4H_9O)_8Ti_3O_2$ and $(n\text{-}C_6H_{13}O)_8Ti_3O_2$ were prepared.

2. Treatment of octaalkoxytrititanoxanes with acetyl chloride yielded compounds of formula:

$$(C_2H_5O)_7Ti_3O_2Cl,\ (C_2H_5O)_6Ti_3O_2Cl_2,$$
$$(n\text{-}C_4H_9O)_6Ti_3O_2Cl_2,\ (n\text{-}C_6H_{13}O)_6Ti_3O_2Cl_2.$$

3. Hexabutoxydichloro- and dichlorohexahexyloxy-trititanoxanes decomposed when heated under reduced pressure with formation of the corresponding trialkoxychlorotitaniums and polymers.

4. Treatment of ethyl orthotitanate with titanium tetrabromide yielded compounds of formula:

$$(C_2H_5O)_2TiBr_2 \text{ and } C_2H_5OTiBr_3.$$

5. By reaction of titanium tetrabromide with ethyl orthotitanate in presence of the calculated amount of piperidine, crystalline double compounds having the following formulas were prepared:

$$(C_2H_5O)_2TiBr_2\cdot C_5H_{10}NH \text{ and } (C_2H_5O)_3TiBr\cdot C_5H_{10}NH.$$

LITERATURE CITED

[1] A. N. Nesmeyanov, R. Kh. Freidlina, and O. V. Nogina, Bull. Acad. Sci. USSR, Div. Chem. 1951 No. 5, 518.

[2] A. N. Nesmeyanov, E. M. Brainina, and R. Kh. Freidlina, Proc. Acad. Sci. USSR 94, No. 2, 249 (1954).

[3] A. N. Nesmeyanov, R. Kh. Freidlina, and E. M. Brainina, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No. 6, 987 (T. p. 861)*

[4] Krautzer, K. M. C. Taggart, Winter, C. A. 42, 1433 (1948) 43, 9026 i (1949).

[5] G. Winter, J. Oil Col. Chem. Assoc. 34, 30 (1951).

[6] N. M. Cullinane, S. Y. Chard, J. Appl. Chem. (London) 1, 400 (1951).

[7] T. Boyd, J. Polymer Sci., 7, No. 6, 591 (1951).

[8] A. N. Nesmeyanov, E. M. Brainina, and R. Kh. Freidlina, Proc. Acad. Sci. USSR 85, No. 3,571 (1952).

[9] O. V. Nogina, R. Kh. Freidlina, and A. N. Nesmeyanov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1950, No. 3, 327.

[10] B. A. Arbuzov and T. G. Shavsha, Proc. Acad. Sci. USSR 68, 859 (1949).

[11] O. V. Nogina, R. Kh. Freidlina, and A. N. Nesmeyanov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, No. 1, 74 (T.p. 81)*.

[12] G. Winter, Paint Notes 5, 285 (1950).

[13] A. N. Nesmeyanov, R. Kh. Freidlina, and O. V. Nogina, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, No. 6, 1038 (T.p. 907).*

[14] J. S. Jennings, W. Wardlaw, W. Y. K. Way, J. Chem. Soc. 1936, 637.

[15] N. M. Cullinane, S. Y. Chard et al. J. Appl. Chem. (London) 2, 250 (1952).

[16] D. C. Bradley, D. C. Hancock, W. Wardlaw, J. Chem. Soc., 1952, 2773.

[17] G. Winter, J. Oil Col. Chem. Assoc. 36, 689 (1953).

Received February 9, 1955

Institute of Heteroorganic Compounds of the USSR Academy of Sciences

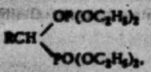
---

* T.p. = C. B. Translation pagination.

SOME DERIVATIVES OF 1-HYDROXYALKYLPHOSPHONIC ACIDS

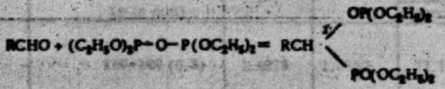
P. I. Alimov and O. N. Fedorova

In 1951 we [1] described a method for the synthesis of some derivatives of 1-hydroxyalkylphosphonic acids of general formula



$$RCH\begin{matrix} \diagup OP(OC_2H_5)_2 \\ \diagdown PO(OC_2H_5)_2 \end{matrix}.$$

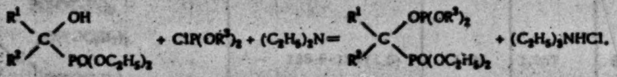
in which R is an aliphatic or aromatic radical. These substances were synthesized by the reaction of tetraethyl pyrophosphite with aldehydes:



$$RCHO + (C_2H_5O)_2P{-}O{-}P(OC_2H_5)_2 = RCH\begin{matrix} \diagup OP(OC_2H_5)_2 \\ \diagdown PO(OC_2H_5)_2 \end{matrix}$$

The aldehydes used were: butyraldehyde, benzaldehyde, p-tolualdehyde, 2-furaldehyde, and acetaldehyde. An attempt to extend this reaction to ketones was not successful: it was found that pyrophosphorous esters do not react with acetone.

In the present paper we describe the synthesis of organophosphorus compounds of this type by the reaction of dialkyl phosphorochloridites with 1-hydroxyalkylphosphonic esters in presence of triethylamine:



$$\begin{matrix} R^1 \diagdown & & \diagup OH \\ & C & \\ R^2 \diagup & & \diagdown PO(OC_2H_5)_2 \end{matrix} + ClP(OR^3)_2 + (C_2H_5)_2N = \begin{matrix} R^1 \diagdown & & \diagup OP(OR^3)_2 \\ & C & \\ R^2 \diagup & & \diagdown PO(OC_2H_5)_2 \end{matrix} + (C_2H_5)_3NHCl.$$

in which R^1 is H or alkyl, and R^2 and R^3 are alkyls. The reaction was carried out in an organic solvent (gasoline, ether) at room temperature, the reaction mixture being finally heated to bring reaction to completion. These derivatives of 1-hydroxyalkylphosphonic acids can be regarded as mixed phosphorous esters, i.e. dialkyl 1-(diethoxyphosphinyl)alkyl phosphites.

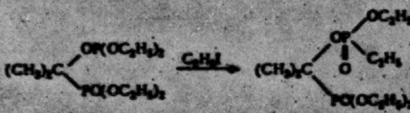
This second method of synthesis became readily accessible when Abramov [2] discovered a simple method for preparing esters of 1-hydroxyalkylphosphonic acids. Whereas the first method was limited to the preparation of compounds of this type from aldehydes and in such a way that all the radicals of the ester groupings were necessarily identical, in the second method ketones can be used as reactants and the radicals of the ester groupings can be the same or different.

We prepared our 1-hydroxyalkylphosphonic esters from diethyl hydrogen phosphite and a carbonyl compound, namely, acetaldehyde, acetone, or 2-butanone. As acid chlorides we used diethyl, dipropyl, and diisobutyl phosphorochloridites.

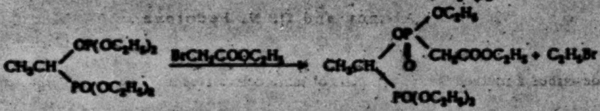
Table 1 gives the formulas, physical constants, and yields of mixed phosphorous esters that we have synthesized by the second method.

The compounds listed in Table 1 are colorless, very mobile liquids having a feeble odor of phosphonic acid derivatives. They are soluble in water and in organic solvents.

Since dialkyl 1-(diethoxyphosphinyl)alkyl phosphites contain one tervalent phosphorus atom attached to ester groupings, they readily undergo isomerization and rearrangement under the action of halo compounds (Arbuzov reaction) with formation of compounds having two quinquevalent phosphorus atoms, for example



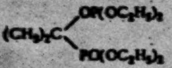
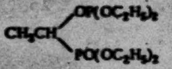
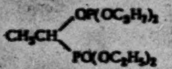
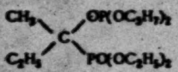
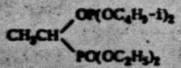
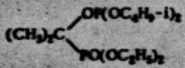
(1)



(2)

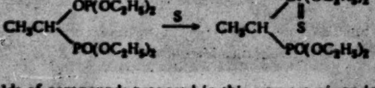
The formulas of substances prepared by this isomerization and rearrangement reaction, together with their physical constants and yields, are given in Table 2.

TABLE 1

Formula	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR		Yield (%)
				Found	Calculated	
	106-107 (0.5)	1.4379	1.0752	77.14	76.98	63.1
	109-110 (1.0)	1.4376	1.0925	72.51	72.37	78.12
	129-130 (1)	1.4395	1.0610	81.89	81.75	50.49
	136.5-138 (1.5)	1.4435	1.057	89.88	90.84	46.65
	128-128.5 (1)	1.4372	1.0345	90.70	90.83	52.25
	126-127 (1)	1.4390	1.0277	95.21	95.46	48.12

The isomerization and rearrangement products of the mixed phosphorous esters are colorless mobile liquids. They have either no odor, or only a very feeble ethereal odor. They are readily soluble in water and in organic solvents.

Sulfur readily adds to dialkyl 1-(diethylphosphinyl)alkyl phosphites with formation of compounds containing two quinquevalent phosphorus atoms, for example:



The formulas, constants, and yields of compounds prepared in this way are given in Table 3.

The organophosphorus compounds listed in Table 3 are colorless mobile liquids having odors characteristic of sulfur compounds. They are sparingly soluble in water, but readily soluble in alcohol and other organic solvents.

TABLE 2

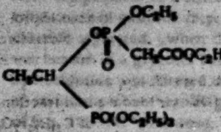
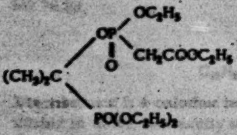
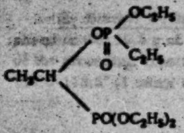
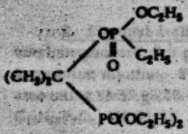
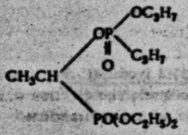
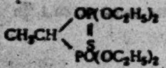
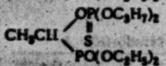
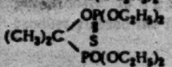
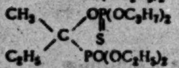
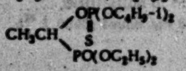
Formula	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR		Yield (%)
				Found	Calculated	
	170-171.5 (1)	1.4425	1.1761	81.07	81.15	54.5
	169-170.5 (1)	1.4450	1.1570	86.03	85.62	47.56
	141.5-143 (1)	1.4370	1.1295	70.05	70.11	81.00
	140-141.5(1)	1.4395	1.1165	74.52	74.73	69.59
	140-142 (0.5)	1.4388	1.0879	79.75	79.49	37.5

TABLE 3

Formula	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR		Yield (%)
				Found	Calculated	
	145-146 (1)	1.4561	1.1526	78.79	78.74	62.72
	156-157 (1)	1.4550	1.1166	87.96	88.12	75.66
	145-146 (1.5)	1.4576	1.1419	83.10	83.35	56.7
	161-162 (1)	1.4598	1.1017	96.92	97.21	36.7
	151-152.5 (1)	1.4525	1.0843	97.12	97.21	65.26

EXPERIMENTAL

Preparation of Dialkyl 1-(Diethoxyphosphinyl)alkyl Phosphites (Table 1)

1. Diethyl 1-(Diethoxyphosphinyl)-1-methylethyl Phosphite. Diethyl phosphorochloridite (15 g) was added at room temperature to a stirred solution of 18.8 g of diethyl 1-hydroxy-1-methylethylphosphonate and 9.7 g of triethylamine in gasoline (b.p. 75-120°). Reaction proceeded with slight evolution of heat, and triethylamine hydrochloride separated. When the whole of the acid chloride had been added, the flask containing the reaction mixture was heated in a glycerol bath at 50-60° for one hour. The mixture was cooled, and the precipitate of triethylamine hydrochloride was filtered off and washed with gasoline. The weight of dry salt was 12.3 g (93.4%), and the weight of reaction product was 30 g. Two distillations of the crude product from an Arbuzov flask yielded a main fraction of b.p. 106-107° (0.5 mm); yield 19.07 g (63.1%); n_D^{20} 1.4379; d_4^{20} 1.0752; found MR 77.14; calculated for $C_{11}H_{26}P_2O_6$ MR 76.98.

Found %: P 19.79; 19.75

$C_{11}H_{26}P_2O_6$. Calculated %: P 19.62

The substance is a colorless mobile liquid having a feeble odor of derivatives of phosphonic acids. It is sparingly soluble in water, but readily soluble in alcohol and gasoline.

2. Diethyl 1-(Diethylphosphinyl)ethyl Phosphite. Reaction was between 18.9 g of diethyl 1-hydroxyethylphosphonate, 10.5 g of diethylamine, and 16.3 g of diethyl phosphorochloridite. The procedure was similar to that of the preceding experiment. Distillation of the crude product yielded 24.5 g (78.12%) of a substance having b.p. 117.5-118.5° (1 mm); n_D^{20} 1.4376; d_4^{20} 1.0925; found MR 72.51; calculated for $C_{10}H_{24}P_2O_6$ MR 72.37.

Found %: P 20.74; 20.62

$C_{10}H_{24}P_2O_6$. Calculated %: P 20.53

3. Dipropyl 1-(Diethoxyphosphinyl)ethyl Phosphite. Reaction was between 16.77 g of diethyl 1-hydroxyethylphosphonate, 9.3 g of diethylamine, and 17 g of dipropyl phosphorochloridite. The reaction was carried out in gasoline solution. Two fractionations of the reaction product from an Arbuzov flask yielded a main fraction amounting to 15 g (50.49%); it had b.p. 129-130° (1 mm); n_D^{20} 1.4395; d_4^{20} 1.0610; found MR 81.89; calculated for $C_{12}H_{28}P_2O_6$ MR 81.75.

Found %: P 19.06; 19.18

$C_{12}H_{28}P_2O_6$. Calculated %: P 18.78

4. Dipropyl 1-(Diethoxyphosphinyl)-1-methylpropyl Phosphite. Reaction was between 21 g of diethyl 1-hydroxy-1-methylpropylphosphonate, 10.1 g of triethylamine, and 18.45 g of dipropyl phosphorochloridite. The reaction was carried out under the conditions described above. The first distillation of the crude product yielded the fractions:

Fraction I, b.p. to 127° (1 mm); 7.5 g
Fraction II, b.p. 127-130° (1 mm); 22.2 g
Residue 3.5 g

Distillation of Fraction II yielded 16.7 g (46.65%) of a substance having b.p. 136.5-138° (1.5 mm); n_D^{20} 1.4435; d_4^{20} 1.0570; found MR 89.88; calculated for $C_{14}H_{32}P_2O_6$ MR 90.84.

Found %: P 17.58; 17.64

$C_{14}H_{32}P_2O_6$. Calculated %: P 17.32

5. Diisobutyl 1-(Diethoxyphosphinyl)ethyl Phosphite. Reaction was between 14 g of diethyl 1-hydroxyethylphosphonate, 16.5 g of diisobutyl phosphorochloridite, and 7.9 g of triethylamine. Fractional distillation of the product yielded the following fractions:

Fraction I, b.p. to 128° (1 mm); 4.5 g
Fraction II, b.p. 128-135° (1 mm); 20.4 g
Residue 3 g

Distillation of Fraction II yielded 14.6 g (52.25%) of a substance having b.p. 128-128.5° (1 mm); n_D^{20} 1.4372; d_4^{20} 1.0345; found MR 90.70; calculated for $C_{14}H_{32}P_2O_6$ MR 90.83.

Found %: P 17.76; 17.71

$C_{14}H_{32}P_2O_6$. Calculated %: P 17.31

6. Diisobutyl 1-(Diethoxyphosphinyl)-1-methylethyl Phosphite. Reaction was between 19.6 g of diethyl 1-hydroxy-1-methylethylphosphonate, 21.25 g of diisobutyl phosphorochloridite, and 10.1 g of triethylamine. Distillation of the product yielded the following fractions:

Fraction I, b.p. 75-130° (1.5 mm); 13.7 g
Fraction II, b.p. 130-135° (1.5 mm); 20.5 g
Residue 1.5 g

Distillation of Fraction II yielded 17.9 g (48.12%) of a substance having b.p. 126-127° (1 mm); n_D^{20} 1.4390; d_4^{20} 1.0277; found MR 95.21; calculated for $C_{15}H_{34}P_2O_6$ MR 95.46.

Found %: P 17.00; 17.02

$C_{15}H_{34}P_2O_6$. Calculated %: P 16.67

Action of Halogen Compounds on Dialkyl 1-(Diethoxyphosphinyl)alkyl Phosphites (Table 2)

1. Action of Ethyl Bromoacetate on Diethyl 1-(Diethylphosphinyl)ethyl Phosphite. Diethyl 1-(diethylphosphinyl)ethyl phosphite (6 g) was introduced into a round-bottomed flask fitted with condenser, thermometer, and dropping funnel. The ester was heated to 120°, and 3.1 g of ethyl bromoacetate was added. The temperature of the reaction mixture rose rapidly to 140°. The ethyl bromide that separated in the course of the reaction was collected in a receiver. The reaction flask was heated for one hour in a bath at 140-145°, and its contents were then distilled. The main fraction, amounting to 3.9 g (54.5%), had b.p. 170-171.5° (1 mm); n_D^{20} 1.4425; d_4^{20} 1.1761; found MR 81.07; calculated for $C_{12}H_{26}P_2O_8$ MR 81.15.

Found %: P 17.57; 17.51

$C_{12}H_{26}P_2O_8$. Calculated %: P 17.22

This substance is a colorless mobile liquid having only a feeble ethereal odor. It is readily soluble in water and organic solvents.

2. Action of Ethyl Bromoacetate on Diethyl 1-(Diethoxyphosphinyl)-1-methylethyl Phosphite. Reaction was between 7.3 g of diethyl 1-(diethoxyphosphinyl)-1-methylethyl phosphite and 3.9 g of ethyl bromoacetate. Evolution of ethyl bromide began at 130°. The temperature of the reaction mixture was raised to 145° and maintained at that level for 45 minutes. Distillation yielded a main fraction, amounting to 3.9 g (47.56%), having b.p. 169-170.5° (1 mm); n_D^{20} 1.4450; d_4^{20} 1.1570; found MR 86.03; calculated for $C_{13}H_{28}P_2O_8$ MR 85.62.

Found %: P 17.10; 17.15

$C_{13}H_{28}P_2O_8$. Calculated %: P 17.32

This substance is a colorless, almost odorless, mobile liquid. It is readily soluble in water and organic solvents.

3. Action of Ethyl Iodide on Diethyl 1-(Diethoxyphosphinyl)ethyl Phosphite. A mixture of 7.9 g of diethyl 1-(diethoxyphosphinyl)ethyl phosphite and 1 ml of ethyl iodide was sealed in a tube and heated for four hours at 135-140°. When the tube was cooled, it was observed that the volume of liquid had diminished somewhat. The contents were transferred to an Arbuzov flask and fractionated. The main fraction, amounting to 6.3 g (81.0%) had b.p. 141.5-143° (1 mm); n_D^{20} 1.4370; d_4^{20} 1.1295; found MR 70.05; calculated for $C_{10}H_{24}P_2O_6$ MR 70.11.

Found %: P 20.20

$C_{10}H_{24}P_2O_6$. Calculated %: P 20.53

4. Action of Ethyl Iodide on Diethyl 1-(Diethoxyphosphinyl)-1-methylethyl Phosphite. A mixture of 7.9 g of diethyl 1-(diethoxyphosphinyl)-1-methylethyl phosphite and 1 ml of ethyl iodide was heated in a sealed tube at 135-140° for four hours. Distillation of the isomerization product yielded 5.4 g (69.6%) of a main fraction having b.p. 140-141.5° (2 mm); n_D^{20} 1.4395; d_4^{20} 1.1165; found MR 74.52; calculated for $C_{11}H_{26}P_2O_6$ MR 74.73.

Found %: P 19.30; 19.25

$C_{11}H_{26}P_2O_6$. Calculated %: P 19.62

This substance is a colorless odorless mobile liquid. It is readily soluble in water and organic solvents.

5. Action of Propyl Bromide on Dipropyl 1-(Diethoxyphosphinyl)ethyl Phosphite. A mixture of 8 g of dipropyl 1-(diethoxyphosphinyl)ethyl phosphite and 1 ml of propyl bromide was heated in a sealed tube at 150-155° for six hours. Distillation from an Arbuzov flask yielded the following fractions:

Fraction I, b.p. 92-137° (1-2 mm); 1 g
Fraction II, b.p. 137-140° (1-0.5 mm); 1.5 g
Fraction III, b.p. 140-142° (0.5 mm); 3 g

Fraction III had n_D^{20} 1.4388; d_4^{20} 1.0879; found MR 79.75; calculated for $C_{12}H_{28}P_2O_6$ MR 79.49.

Found %: P 18.39; 18.29

$C_{12}H_{28}P_2O_6$. Calculated %: P 18.23

Addition of Sulfur to Dialkyl 1-(Diethoxyphosphinyl)alkyl Phosphites (Table 3)

1. Addition of Sulfur to Diethyl 1-(Diethoxyphosphinyl)ethyl Phosphite. A mixture of 10 g of diethyl 1-(diethoxyphosphinyl)ethyl phosphite, 1.06 g of sulfur powder, and 10 ml of benzene was prepared in a flask fitted with reflux condenser. The reaction mixture was heated for some time at the boiling point of benzene. The solvent was then removed, and the residue was vacuum-distilled. The main fraction, amounting to 6.9 g (62.72%), had b.p. 145-146° (1 mm); n_D^{20} 1.4561; d_4^{20} 1.1528; found MR 78.79; calculated for $C_{10}H_{24}P_2O_6S$ MR 78.74.

Found %: P 18.89; 18.85; S 9.48; 9.68

$C_{10}H_{24}P_2O_6S$. Calculated %: P 18.56; S 9.58

This substance is a colorless mobile liquid having a feeble sulfur-compound odor. It is readily soluble in organic solvents, but sparingly soluble in water,

2. Addition of Sulfur to Dipropyl 1-(Diethoxyphosphinyl)ethyl Phosphite. Reaction was between 10 g of the mixed phosphorous ester, 0.97 g of sulfur, and 10 ml of benzene. Distillation of the crude product yielded 8.3 g (75.66%) of a substance having b.p. 156-157° (1 mm); n_D^{20} 1.4550; d_4^{20} 1.1166; found MR 87.96; calculated for $C_{12}H_{28}P_2O_6S$ MR 88.12.

Found %: P 17.53; 17.52

$C_{12}H_{28}P_2O_6S$. Calculated %: P 17.13

This compound is a colorless mobile liquid having a sulfur-compound odor. It is very sparingly soluble in water, but readily soluble in organic solvents.

3. Addition of Sulfur to Diethyl 1-(Diethoxyphosphinyl)-1-methylethyl Phosphite. Sulfur (0.81 g) was sprinkled in small portions into a solution of 8 g of diethyl 1-(diethoxyphosphinyl)-1-methylethyl phosphite in 8 ml of benzene. The temperature rose by 8°. The reaction flask was heated in a glycerol bath at 50-90°. After some time the whole of the sulfur went into solution. The solvent was distilled off, and the reaction product was vacuum-distilled, when it yielded the fractions:

Fraction I, b.p. 105-138° (3-2 mm); 0.5 g
Fraction II, b.p. 138-145° (1.5 mm); 0.5 g
Fraction III, b.p. 145-146° (1.5 mm); 5 g

Fraction III, obtained in 56.7% yield, had n_D^{20} 1.4576; d_4^{20} 1.1419; found MR 83.1; calculated for $C_{11}H_{26}P_2O_6S$ MR 83.35.

Found %: P 17.86; 18.06

$C_{11}H_{26}P_2O_6S$. Calculated %: P 17.81

4. Addition of Sulfur to Dipropyl 1-(Diethoxyphosphinyl)-1-methylpropyl Phosphite. Sulfur (0.7 g) was added to a solution of 8 g of dipropyl 1-(diethoxyphosphinyl)-1-methylpropyl phosphite in 10 ml of benzene. The mixture was heated for a short time, the benzene was distilled off, and the residue was vacuum-fractionated. The following fractions were obtained.

Fraction I, b.p. 95-155° (2-1 mm); 1.4 g
Fraction II, b.p. 155-161° (1 mm); 0.5 g
Fraction III, b.p. 161-162° (1 mm); 3.2 g
Residue 1 g

The yield of Fraction III was 36.7%. It had n_D^{20} 1.4598; d_4^{20} 1.1017; found MR 96.92; calculated for $C_{14}H_{32}P_2O_6S$ MR 97.21.

Found %: P 15.82; 15.70; S 8.12; 8.10

$C_{14}H_{32}P_2O_6S$. Calculated %: P 15.89; S 8.2

This substance is a colorless mobile liquid having a sulfur-compound odor. It is soluble in water, and very readily soluble in alcohol, benzene, and other organic solvents.

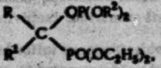
5. Addition of Sulfur to Diisobutyl 1-(Diethoxyphosphinyl)ethyl Phosphite. Reaction was between 10 g of diisobutyl 1-(diethoxyphosphinyl)ethyl phosphite and 0.86 g of sulfur; it was carried out in benzene solution. Distillation of the product yielded a main fraction, amounting to 7.1 g (65.26%); having b.p. 151-152.5° (1 mm); n_D^{20} 1.4525; d_4^{20} 1.0843; found MR 97.12; calculated for $C_{14}H_{32}P_2O_6S$ MR 97.21.

Found %: P 16.30; 16.21

$C_{14}H_{32}P_2O_6S$. Calculated %: P 15.89

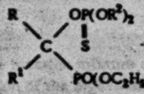
SUMMARY

1. By the action of dialkyl phosphorochloridites on 1-hydroxyalkylphosphonic esters in presence of triethylamine, some mixed phosphorous esters were obtained, namely, dialkyl 1-(diethoxyphosphinyl)alkyl phosphites of general formula:

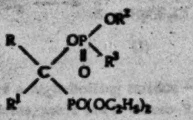


in which R is H or alkyl, and R^1 and R^2 are alkyls.

2. From these substances, by the action of sulfur and by the action of halogen compounds, two series of substances having the following formulas were prepared:



;



and their physical constants were determined.

LITERATURE CITED

[1] A. E. Arbuzov and P. I. Alimov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1951, No. 5, 530.

[2] V. S. Abramov, J. Gen. Chem., 22, 4, 647 (1952)(T. p. 709)*.

Received September 22, 1954

A. E. Arbuzov Chemical Institute of the Kazan Affiliated Institute of the USSR Academy of Sciences

---

* T. p. = C. B. Translation pagination.

ADDITION REACTIONS OF PERFLUOROOLEFINS

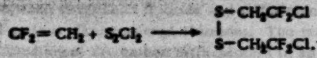
COMMUNICATION 4. REACTION OF VINYLIDENE FLUORIDE WITH SULFUR CHLORIDES AND WITH ALKANESULFENYL CHLORIDES

I. L. Knunyants and E. G. Vykhovskaya

In the preceding communication [1] the products of the addition of sulfur chlorides to tetrafluoroethylene were described. In the present paper we report the results of a study of the reaction of vinylidene fluoride with sulfur chlorides and with alkanesulfenyl chlorides.

The reaction between sulfur dichloride and vinylidene fluoride was carried out in a medium of dry carbon tetrachloride in a rotating steel autoclave. From the reaction mixture we succeeded in isolating bis(2-chloro-2,2-difluoroethyl) disulfide (I) in 15-20% yield. The fraction coming over before the disulfide contained several substances that were able to liberate iodine from acidified potassium iodide solution and to add vigorously to cyclohexene, but we did not succeed in isolating any individual substances from this fraction.

The reaction between vinylidene fluoride and sulfur monochloride proceeded in a more simple fashion. Thus, when the reactants were heated in a medium of dry carbon tetrachloride at 100° for 3-4 hours in a rotating steel autoclave (in presence of traces of hydroquinone), the same bis(2-chloro-2,2-difluoroethyl) disulfide (I) was isolated in 65-70% yield (calculated on the amount of vinylidene fluoride that reacted):



$$CF_2{=}CH_2 + S_2Cl_2 \longrightarrow \begin{matrix} S-CH_2CF_2Cl \\ | \\ S-CH_2CF_2Cl. \end{matrix}$$

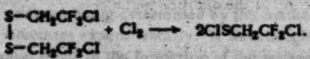
(I)

In addition to the disulfide, the reaction mixture contained a high-boiling residue — probably a mixture of polysulfides. By careful fractionation of the high-boiling products, some bis(2-chloro-2,2-difluoroethyl) trisulfide was isolated:

$$S_3(CH_2CF_2Cl)_2.$$

(II)

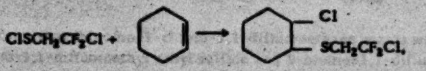
In order to prove the structure of bis(2-chloro-2,2-difluoroethyl) disulfide, it was treated with chlorine:



$$\begin{matrix} S-CH_2CF_2Cl \\ | \\ S-CH_2CF_2Cl \end{matrix} + Cl_2 \longrightarrow 2ClSCH_2CF_2Cl.$$

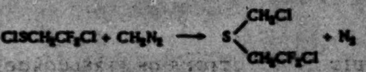
(III)

The 2-chloro-2,2-difluoroethanesulfenyl chloride (III) then formed was found to undergo many reactions characteristic of alkanesulfenyl chlorides. Thus, treatment with cyclohexene yielded 2-chlorocyclohexyl 2-chloro-2,2-difluoroethyl sulfide:



(IV)

and treatment with an ethereal solution of diazomethane yielded 2-chlorocyclohexyl chloromethyl sulfide:



$$ClSCH_2CF_2Cl + CH_2N_2 \longrightarrow S\begin{matrix} CH_2Cl \\ CH_2CF_2Cl \end{matrix} + N_2$$

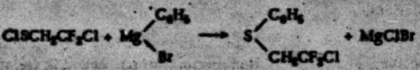
(V)

When an ethereal solution of the sulfenyl chloride was treated with diethylamine, the corresponding sulfenamide (VI) was readily formed:

$$ClSCH_2CF_2Cl + 2(C_2H_5)NH \longrightarrow (C_2H_5)_2NSCH_2CF_2Cl + (C_2H_5)_2NH \cdot HCl.$$

(VI)

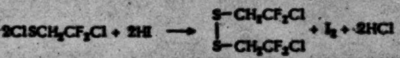
Reaction of 2-chloro-2,2-difluoroethanesulfenyl chloride with phenylmagnesium bromide yielded 2-chloro-2,2-difluoroethyl phenyl sulfide:



$$ClSCH_2CF_2Cl + Mg\begin{matrix} C_6H_5 \\ Br \end{matrix} \longrightarrow S\begin{matrix} C_6H_5 \\ CH_2CF_2Cl \end{matrix} + MgClBr$$

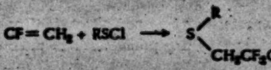
(VII)

Treatment of an ethereal solution of 2-chloro-2,2-difluoroethanesulfenyl chloride with aqueous potassium iodide resulted in the formation of bis(2-chloro-2,2-difluoroethyl) disulfide:



$$2ClSCH_2CF_2Cl + 2HI \longrightarrow \begin{matrix} S-CH_2CF_2Cl \\ | \\ S-CH_2CF_2Cl \end{matrix} + I_2 + 2HCl$$

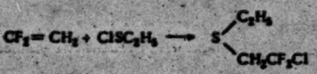
Apart from the addition reactions between vinylidene fluoride and sulfur chlorides, we carried out addition reactions between vinylidene fluoride and various alkanesulfenyl chlorides. The reaction was generally carried out by heating the reactants together in a medium of dry carbon tetrachloride in an autoclave; it resulted in the formation of the corresponding sulfides:



$$CF = CH_2 + RSCl \longrightarrow S\begin{matrix} R \\ CH_2CF_2Cl \end{matrix}$$

In this way we prepared 2-chloro-2,2-difluoroethyl ethyl sulfide ($R = C_2H_5$), 2-chloroethyl 2-chloro-2,2-difluoroethyl sulfide ($R = CH_2CH_2Cl$), 2-chloro-2,2-difluoroethyl 2-chloropropyl sulfide ($R = CH_2CHCl-CH_3$), and bis(2-chloro-2,2-difluoroethyl) sulfide ($R = CH_2CF_2Cl$); experiment showed that the last compound cannot be obtained by the direct reaction of vinylidene fluoride with sulfur chlorides.

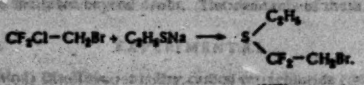
In spite of the almost complete absence of doubt about the structures of the sulfides obtained – the mechanism of their formation and the direction of the addition being determined by the marked polarity of the starting substances – it was desirable to confirm their structures experimentally. It was thought that the reaction of 2-bromo-1-chloro-1,1-difluoroethane with thiols should result in the formation of the sulfide that was obtained also by reaction of vinylidene fluoride with ethanesulfenyl chloride:



$$CF_2 = CH_2 + ClSC_2H_5 \longrightarrow S\begin{matrix} C_2H_5 \\ CH_2CF_2Cl \end{matrix}$$

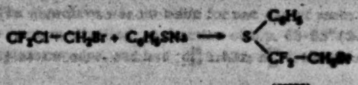
(VIII)

Experiment showed, however, that 2-bromo-1-chloro-1,1-difluoroethane reacts with benzene- and ethane-thiols with formation of 2-bromo-1,1-difluoroethyl ethyl sulfide and 2-bromo-1,1-difluoroethyl phenyl sulfide, respectively:



$$CF_2Cl-CH_2Br + C_2H_5SNa \longrightarrow S\begin{cases}C_2H_5\\ CF_2-CH_2Br.\end{cases}$$

(XII)

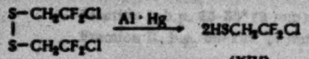


$$CF_2Cl-CH_2Br + C_6H_5SNa \longrightarrow S\begin{cases}C_6H_5\\ CF_2-CH_2Br\end{cases}$$

(XIII)

The bromine atom of 2-bromo-1-chloro-1,1-difluoroethane is found to be very greatly stabilized by the neighboring chlorodifluoromethyl group. The stabilization of bromine by proximity with a chlorodifluoromethyl group has been observed several times previously [2].

The direction of the addition of sulfur chlorides to vinylidene fluoride was proved conclusively by the formation of 2-chloro-2,2-difluoroethanethiol as the result of the reduction of bis(2-chloro-1,1-difluoroethyl) disulfide with amalgamated aluminum in a medium of moist ether:

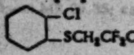


$$\begin{array}{l}S-CH_2CF_2Cl\\ |\\ S-CH_2CF_2Cl\end{array} \xrightarrow{Al\cdot Hg} 2HSCH_2CF_2Cl$$

(XIV)

2-Chloro-2,2-difluoroethanethiol was found to be quite stable; it is a colorless mobile liquid having the unpleasant odor that is characteristic of thiols. The formation of a stable compound could scarcely be expected if addition is in the opposite direction, since not a single compound is known in which two fluorine atoms and a hydroxyl or thiol group are to be found on the same carbon atom.

TABLE

Formula of compound	B.p. in °C(p in mm)	d_4^{20}	Refractive index n_D^{20}
$\begin{array}{l}S-CH_2CF_2Cl\\ |\\ S-CH_2CF_2Cl\end{array}$	62 (3)	1.531	1.4500
$S_2(CH_2CF_2Cl)_2$	93-95 (7)	1.588	1.494
$ClSCH_2CF_2Cl$	110-112	1.523	1.448
	129-130 (9)	1.324	1.4870
$CH_2ClSCH_2CF_2Cl$	57-58 (25)	1.468	1.5550
$(C_2H_5)_2NSCH_2CF_2Cl$	52-54 (7)	1.169	1.4370
$C_6H_5SCH_2CF_2Cl$	103-104 (11)	1.313	1.5270
$C_2H_5SCH_2CF_2Cl$	35 (30)	1.205	1.4340
$CH_2ClCH_2SCH_2CF_2Cl$	55-56 (7)	1.4237	1.4650
$CH_3CHClCH_2SCH_2CF_2Cl$	93 (5)	1.390	1.4825
$CF_2ClCH_2SCH_2CF_2Cl$	78 (50)	1.526	1.4200
$C_2H_5SCF_2CH_2Br$	67-68 (32)	1.505	1.469
$C_6H_5SCF_2CH_2Br$	123 (14)	1.553	1.540
$HSCH_2CF_2Cl$	75-76	1.344	1.405

It was in fact found that no 2-chloro-2,2,1,1-tetrafluoroethanethiol could be obtained by the reduction of bis(2-chloro-2,2,1,1-tetrafluoroethyl) disulfide; in this reaction sulfur was precipitated and resinous products were formed.

The structures of our products are therefore beyond doubt. The constants of these compounds are given in the table.

EXPERIMENTAL

Bis(2-chloro-2,2-difluoroethyl) Disulfide. a) Dry carbon tetrachloride (30 ml) and sulfur dichloride (10 g) were introduced into a 100-ml rotating steel autoclave. The autoclave was then cooled, and 13 g of liquid vinylidene fluoride was introduced. The autoclave was set aside for one day at room temperature. The solvent was distilled off, and the residue was vacuum-distilled. A fraction of b.p. 63-65° (3 mm) was collected (20% yield). It was a clear colorless liquid of unpleasant odor, and had d_{20}^{20} 1.531; n_D^{20} 1.4500; found MR 46.01; calculated for $C_4H_4F_4Cl_2S$ MR 46.16.

Found %: Cl 26.90; F 29.66; S 24.10

$C_4H_4F_4Cl_2S$. Calculated %: Cl 26.99; F 28.90; S 24.30

b) A mixture of 12 g of sulfur monosulfide, 0.1 g of hydroquinone, and 15 ml of dry carbon tetrachloride was prepared in a 100 ml stainless steel autoclave. The autoclave was cooled, and 15 g of vinylidene fluoride was introduced. The autoclave was then heated at 90-100° for 4-6 hours with constant rotation. After removal of unchanged olefin and solvent by distillation, the residue was vacuum-fractionated:

Fraction I, b.p. 63-65° (3 mm); yield 15 g (65%)
Fraction II, b.p. 80-120° (4 mm); yield 3 g

Fraction I was bis(2-chloro-2,2-difluoroethyl) disulfide — a colorless very mobile liquid of unpleasant odor; d_{20}^{20} 1.533; n_D^{20} 1.4500.

Bis(2-chloro-2,2-difluoroethyl) Trisulfide. The residue remaining after the removal of the disulfide by distillation was repeatedly fractionated. A fraction boiling at 93-95° (7 mm) was collected; it was a clear yellowish liquid of unpleasant odor: d_{20}^{20} 1.588; n_D^{20} 1.494; found MR 54.07; calculated for $C_4H_4F_4Cl_2S_3$ MR 54.48.

Found %: Cl 23.78; F 24.70; S 32.05

$C_4H_4F_4Cl_2S_3$. Calculated %: Cl 24.07; F 25.76; S 32.54

2-Chloro-2,2-difluoroethanesulfenyl Chloride. Bis(2-chloro-2,2-difluoroethyl) disulfide (12 g) was introduced into a round-bottomed flask provided with a calcium chloride tube and a tube for the passage of gas. A stream of dry chlorine was passed in until the increase in weight was 3 g. Reaction was accompanied by the evolution of much heat. The solution acquired a deep orange color. The reaction mixture was fractionated through a column at atmospheric pressure. An 80% yield of 2-chloro-2,2-difluoroethanesulfenyl chloride, b.p. 110-112° was obtained. It is a bright-yellow, readily mobile liquid having a sharp odor typical of sulfenyl chlorides: d_{20}^{20} 1.523; n_D^{20} 1.448, found MR 29.35; calculated for $C_2H_2F_2Cl_2S$ MR 29.09.

Found %: active Cl 21.98; total Cl 42.35; F 22.66; S 19.61

$C_2H_2F_2Cl_2S$. Calculated %: active Cl 21.24; total Cl 42.51; F 22.75; S 19.16

Bis(2-chloro-2,2-difluoroethyl) Disulfide. A solution of 10 g of 2-chloro-2,2-difluoroethanesulfenyl chloride in ether was introduced into a separating funnel, and an excess of 10% aqueous potassium iodide was added in small portions. The ether solution was separated, washed with thiosulfate solution until colorless, and dried with sodium sulfate. The ether was distilled off, and the residue was distilled under reduced pressure. Two distillations yielded the pure disulfide in 85% yield. It had b.p. 62° (3 mm), d_{20}^{20} 1.53 and n_D^{20} 1.452.

2-Chlorocyclohexyl 2-Chloro-2,2-difluoroethyl Sulfide. 2-Chloro-2,2-difluoroethanesulfenyl chloride (6 g) was added slowly with shaking to excess of cyclohexene. The color of the sulfenyl chloride disappeared immediately, and much heat was evolved. The excess of cyclohexene was distilled off, and the residue was vacuum-distilled. After the second distillation the boiling point of the product was 129-130° (9 mm); it had d_{20}^{20} 1.324; n_D^{20} 1.487; found MR 54.13; calculated for $C_8H_{12}F_2Cl_2S$ MR 54.17.

Found %: Cl 28.28; F 15.13; S 13.22

$C_8H_{12}F_2Cl_2S$. Calculated %: Cl 28.50; F 15.26; S 12.85

2-Chloro-2,2-difluoroethyl Chloromethyl Sulfide. At −5°, an ethereal solution of 2-chloro-2,2-difluoroethanesulfenyl chloride was slowly added to an excess of ethereal diazomethane. The excess of diazomethane was distilled off, and the residue was vacuum-distilled. The product, which was obtained in 50% yield, boiled at 57-59° (25 mm). It is a colorless pleasant-smelling liquid; d_{20}^{20} 1.468; n_D^{20} 1.555; found MR 33.45; calculated for $C_3H_4F_2Cl_2S$ MR 33.70.

Found %: Cl 38.86; F 22.09; S 17.90

$C_3H_4F_2Cl_2S$. Calculated %: Cl 39.22; F 21.00; S 17.68

2-Chloro-N,N-diethyl-2,2-difluoroethanesulfenamide. A mixture of 11.5 g of 2-chloro-2,2-difluoroethanesulfenyl chloride and 70 ml of dry ether was prepared in a round-bottomed flask fitted with dropping funnel and reflux condenser, and a solution of 10 g of diethylamine in 60 ml of dry ether was added slowly. The precipitated diethylamine hydrochloride was filtered off, ether was distilled off, and the residue was distilled at reduced pressure. The product, obtained in 65% yield after the second distillation, boiled at 52-54° (7 mm) and had d_{20}^{20} 1.169; n_D^{20} 1.437; found MR 45.61; calculated for $C_6H_{12}NF_2ClS$ MR 46.10.

Found %: Cl 17.88; F 18.89; S 16.10

$C_6H_{12}NF_2ClS$. Calculated %: Cl 17.45; F 18.64; S 15.72

2-Chloro-2,2-difluoroethyl Phenyl Sulfide. Magnesium (1.8 g) and iodine (one crystal) were introduced into a round-bottomed flask fitted with stirrer, dropping funnel, and reflux condenser. A solution of 11 g of bromobenzene in ether was added gradually from the dropping funnel. When the whole of the bromobenzene had been added, the reaction mixture was heated at 40° for 30 minutes. Then, with cooling and stirring, a solution of 9 g of 2-chloro-2,2-difluoroethanesulfenyl chloride in dry ether was added. The reaction mixture was poured into water, and the ether layer was separated and dried with magnesium sulfate. Ether was distilled off, and the residue was fractionated at reduced pressure. The second distillation gave a colorless mobile liquid having a sharp unpleasant odor. It was obtained in 45% yield and had b.p. 103-104° (11 mm), d_{20}^{20} 1.313; n_D^{20} 1.5270; found MR 48.33; calculated for $C_8H_7F_2ClS$ MR 47.90.

Found %: Cl 17.20; F 18.60; S 15.34

$C_8H_7F_2ClS$. Calculated %: Cl 17.00; F 18.20; S 15.96

2-Chloro-2,2-difluoroethyl Ethyl Sulfide. A mixture of 11 g of ethanesulfenyl chloride and 11 g of liquid vinylidene fluoride was prepared in rotating steel autoclave. The autoclave was heated at 65-70° for eight hours with constant rotation. Unchanged vinylidene fluoride was distilled off, and the residue was distilled under reduced pressure. The second distillation gave 2-chloro-2,2-difluoroethyl ethyl sulfide in 20% yield. It is a highly mobile colorless liquid, b.p. 35° (30 mm), d_{20}^{20} 1.216; n_D^{20} 1.4276; found MR 33.34; calculated for $C_4H_7F_2ClS$ MR 33.04.

Found %: Cl 21.72; F 23.00; S 20.34

$C_4H_7F_2ClS$. Calculated %: Cl 22.11; F 23.67; S 19.93

2-Chloroethyl 2-Chloro-2,2-difluoroethyl Sulfide. A mixture of 20 ml of dry carbon tetrachloride, 10 g of 2-chloroethanesulfenyl chloride, and 10 g of vinylidene fluoride was prepared in a steel autoclave. The autoclave was heated at 60° for ten hours. Unchanged olefin and solvent were distilled off, and the residue was vacuum-distilled. The second distillation gave a slightly yellowish, readily mobile liquid having a feeble unpleasant odor. It was obtained in 35% yield and had b.p. 55-56° (7 mm), d_{20}^{20} 1.4237; n_D^{20} 1.4650; found MR 37.86; calculated for $C_4H_6F_2ClS$ MR 37.87.

Found %: Cl 36.71; F 19.55; S 16.36

$C_4H_6F_2Cl_2S$. Calculated %: Cl 36.41; F 19.48; S 16.41

2-Chloro-2,2-difluoroethyl 2-Chloropropyl Sulfide. A mixture of 20 ml of dry carbon tetrachloride, 13 g of 2-chloropropanesulfenyl chloride, and 10 g of vinylidene fluoride was prepared in an autoclave. The autoclave was heated at 100° for nine hours. Unchanged olefin and solvent were distilled off, and the residue was vacuum-distilled. The third distillation gave a substance boiling at 93° (5 mm) in 15% yield; a colorless readily mobile liquid having a feeble unpleasant odor; d_{20}^{20} 1.3903; n_D^{20} 1.4825; found MR 42.89; calculated for $C_5H_8F_2Cl_2S$ MR 42.50.

Found %: Cl 33.76; F 17.80; S 17.22

$C_5H_8F_2Cl_2S$. Calculated %: Cl 33.97; F 18.18; S 16.64

Bis(2-chloro-2,2-difluoroethyl) Sulfide. A mixture of 20 ml of dry carbon tetrachloride, 13 g of 2-chloro-2,2-difluoroethanesulfenyl chloride, and 10 g of vinylidene fluoride was prepared in a stainless steel autoclave. The autoclave was heated at 90-95° for five hours. After removal of unchanged vinylidene fluoride and solvent by distillation, the residue was vacuum-distilled. The third distillation gave a product boiling at 78° (50 mm) in 50% yield. It was a very mobile colorless liquid having a very unpleasant odor; it had d_{20}^{20} 1.526; n_D^{20} 1.4200; found MR 37.69; calculated for $C_4H_4F_4Cl_2S$ MR 38.30.

Found %: Cl 30.81; F 32.25; S 14.42

$C_4H_4F_4Cl_2S$. Calculated %: Cl 30.74; F 32.90; S 13.85

A weighed amount of bis(2-chloro-2,2-difluoroethyl) sulfide and some alcoholic potash were introduced into a round-bottomed flask fitted with a reflux condenser. The mixture was heated for 40 minutes in a boiling water bath, and was then titrated for chloride by the Volhard method:

Found %: Cl 30.90

Calculated %: Cl 30.74

2-Bromo-1,1-difluoroethyl Ethyl Sulfide. A mixture of 30 ml of absolute methanol, 1.5 g of sodium, and 4 g of ethanethiol was prepared in flask fitted with reflux condenser and dropping funnel. 2-Bromo-1-chloro-1,1-difluoroethane (12 g) was then added slowly. The reaction mixture was heated for two hours in a water bath. The precipitated sodium chloride was then filtered off, and the residue was distilled under reduced pressure. After a second distillation the boiling point of the product was 67-68° (32 mm); it had d_{20}^{20} 1.505; n_D^{20} 1.469.

Found %: Br 39.10; F 18.07; S 15.83

$C_4H_7F_2BrS$. Calculated %: Br 39.02; F 17.07; S 15.61

2-Bromo-1,1-difluoroethyl Phenyl Sulfide. A mixture of 30 ml of absolute alcohol, 2.5 g of sodium, and 12 g of benzenethiol was prepared in a flask fitted with reflux condenser and dropping funnel. 2-Bromo-1-chloro-1,1-difluoroethane (20 g) was then added slowly. The reaction mixture was heated for one hour in a water bath, and was then poured into water. The precipitated oil was separated, washed with sodium bicarbonate solution and then water, dried, and distilled. The product was a pleasant-smelling colorless liquid boiling at 123° (14 mm) after the second distillation; it had d_{20}^{20} 1.553; n_D^{20} 1.540; found MR 51.10; calculated for $C_8H_7F_2BrS$ MR 50.90.

Found %: S 12.43; F 14.69; Br 32.02

$C_8H_7F_2BrS$. Calculated %: S 12.64; F 15.02; Br 31.65

2-Chloro-2,2-difluoroethanethiol. Bis(2-chloro-2,2-difluoroethyl) disulfide (6 g) was added to a suspension of amalgamated aluminum turnings in moist ether. Vigorous reaction was observed. The flask was allowed to stand at room temperature for two hours. Aluminum hydroxide was then filtered off, and the reaction mixture was distilled through an efficient column. The products were 2 g of a substance boiling at 75-76° and 3 g of unchanged disulfide [b.p. 62-64° (4 mm); d_{20}^{20} 1.530]. The substance of b.p. 75-76° was a very mobile colorless liquid having a sharp unpleasant odor typical of thiols. It gave a positive test for the thiol group. The yield, calculated on the amount of disulfide that reacted, was 70%. The substance had d_{20}^{20} 1.344; n_D^{20} 1.405; found MR 24.16; calculated for $C_2H_3F_2ClS$ MR 24.03.

Found %: Cl 27.20; F 28.55; S 24.10

$C_2H_3F_2ClS$. Calculated %: Cl 26.79; F 28.68; S 24.15

SUMMARY

1. By the addition of sulfur chlorides and of alkanesulfenyl chlorides to vinylidene fluoride, some new sulfenyl chlorides, sulfides, and polysulfides containing the 2-chloro-2,2-difluoroethyl group were obtained.

2. 2-Chloro-2,2-difluoroethanethiol was prepared by the reduction of bis(2-chloro-2,2-difluoroethyl) disulfide. 2-Bromo-1,1-difluoroethyl alkyl sulfides were prepared by the reaction of 2-bromo-1-chloro-1,1-difluoroethane with thiols.

Received May 20, 1954

LITERATURE CITED

[1] I. L. Knunyants and A. V. Fokin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 4, 705 (T.p.627)*.

[2] E. T. McBee, Ind. Eng. Chem., 39, 236, (1947).

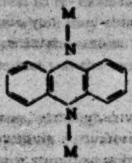
---

* T. p. = C. B. Translation pagination.

COMPLEX NATURE OF DIMETAL COMPOUNDS OF PHENAZINE

B. M. Mikhailov and A. N. Blokhina

We have established previously that phenazine readily forms compounds with alkali metals when 1,2-dimethoxyethane is used as solvent [1]. In presence of this solvent we succeeded in effecting the direct addition of sodium to phenazine, and we obtained the dilithium compound of phenazine by the metallization of 5,10-dihydrophenazine with phenyllithium. At that time the products were not isolated in the individual state and were not analyzed; their structure, as products of the addition of two metal atoms at the nitrogen atoms – i.e. as

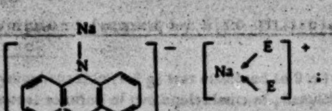


(I)

in which M is an alkali-metal atom – was assumed on the basis of their chemical reactions with various reagents (alkyl halides, ethylene oxide, etc.). In view of recent results relating to the complex nature of dimetal derivatives of unsaturated systems [2], the question arose of the investigation of the composition and structure of the dimetal compounds of phenazine.

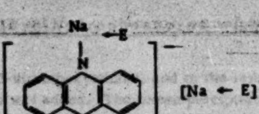
The disodium compound was prepared for analysis by metallization of 5,10-dihydrophenazine with aid of 9,10-disodio-9,10-dihydroanthracene in 1,2-dimethoxyethane. This method is to be preferred to the direct addition of sodium to phenazine [1] in that it ensures the absence of admixture of fine particles of metal to the metal compound of phenazine. The dilithium compound was prepared in the same medium by the metallization of 5,10-dihydrophenazine with phenyllithium. Analysis of the dimetal compounds of phenazine for their contents of metal and phenazine showed that coordinated 1,2-dimethoxyethane was present – two molecules in the sodium compound, and six molecules in the lithium compound.

It follows from the fact that in 1,2-dimethoxyethane the dimetal compounds of phenazine conduct electricity that these compounds are ionized. On analogy with the dimetal compounds of anthracene and other unsaturated systems [2] it must be supposed that only one of the metal atoms is in the ionized state, whereas the other is attached to the heterocycle by a covalency. The structure of the disodium compound can then be represented by formula (II) or (III):



(II)

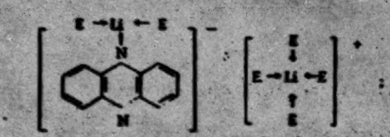
;



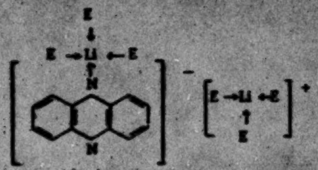
(III)

in which $E = CH_3OCH_2{-}CH_2{-}OCH_3$.

For the structure of the dilithium compound two variants (IV) and (V) are again possible, the difference lying in the disposition of the diether molecules:



(IV)



(V)

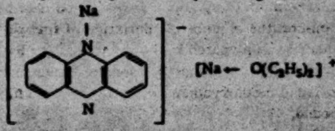
in which $E = CH_3OCH_2CH_2OCH_3$.

Since the metal ion has the greater tendency to undergo coordination, the more probable structure for the dilithium compound of phenazine is (IV), in which the metal ion is coordinately saturated.

In connection with the establishment of the complex nature of the dimetal compounds of phenazine prepared in a 1,2-dimethoxyethane medium, it was of interest to re-examine Schlenk and Bergmann's results [3] on the composition of the sodium compound of phenazine which they obtained in an ether medium by the action of the disodium derivative of N-(diphenylmethylene)aniline on phenazine. They assumed, solely on the basis of the determination of the metal content (11.3%) that the product was the molecular compound formed by 9,10-disodio-9,10-dihydrophenazine with a molecule of phenazine.

The authors did not describe their experiments, although it was essential to do so. On repeating their work, we found that, when only a slight excess of the disodium derivative of N-(diphenylmethylene)aniline is used, the metal contents of the products vary greatly from one experiment to another; reproducible results are obtained only when a large excess of this reagent is used. Under these conditions, a substance containing 15.6-16% of sodium and 61-62% of phenazine is obtained, whereas, for a molecular compound of disodiodihydrophenazine with phenazine such as Schlenk and Bergmann thought they had obtained, the sodium content should be 11.33% and the phenazine content 88.67%.

The metal and phenazine contents of our phenazine disodium compound correspond to a monoetherate, which, by analogy with the above-described complex compounds, may be assigned the following structure (VI):



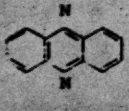
(VI)

EXPERIMENTAL

All operations were carried out in an atmosphere of nitrogen. The metal compounds of phenazine were prepared in two-legged tubes.

Complex Compound formed by 5,10-Dilithio-5,10-dihydrophenazine with 1,2-Dimethoxyethane

5,10-Dihydrophenazine (0.6 g) was dissolved in 9 ml of 1,2-dimethoxyethane, and to the resulting solution 30 ml of an ethereal solution of two equivalents of phenyllithium was added. The brown precipitate that separated was filtered off through a special filter funnel [4], washed with 1,2-dimethoxyethane, and dried to constant weight in a vacuum. The complex was then covered with a layer of ether, and an ethereal solution of methanol was added. Water was then added, and the metal content of the aqueous layer was determined. Solvent was distilled from the ethereal layer, and the residue was dried to constant weight in a vacuum desiccator. The difference between the weight of the complex and the sum of the weights of phenazine (obtained in the form of 5,10-dihydrophenazine) and lithium was equal to the weight of the coordinately bound 1,2-dimethoxyethane.



$\cdot 2Li \cdot 6C_4H_{10}O_2$.

Found %: Li 2.08; 2.06; phenazine 24.83; 25.11

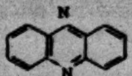
Calculated %: Li 1.89; phenazine 24.52

The following results were obtained for the conductance of the dilithium compound of phenazine in 1,2-dimethoxyethane: molar volume g = 565 liters, specific conductance $\kappa = 4.47 \cdot 10^{-6}$ cm^{-1}·ohm^{-1}, molar conductance $\lambda = 0.252$ cm^{-1}ohm^{-1}.

Complex Compound formed by 5,10-Disodium-5,10-dihydrophenazine with 1,2-dimethoxyethane

A solution of 0.7 g of dihydrophenazine in 10 ml of 1,2-dimethoxyethane was added to a filtered solution of the disodium compound of anthracene prepared by shaking a mixture of 1 g of anthracene, 0.3 g of sodium, and 15 ml of 1,2-dimethoxyethane for 25 hours. The brick-red precipitate was filtered off, washed with 1,2-dimethoxyethane, dried to constant weight, and analyzed as described above.

Found %: Na 10.90; 11.05; phenazine 46.25; 45.00



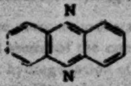
$2Na \cdot 2C_4H_{10}O_2$. Calculated %: Na 11.32; phenazine 44.34

The following results were obtained for the conductance of the disodium compound of phenazine in 1,2-dimethoxyethane: molar volume g = 160 liters, specific conductance $\kappa = 5.16 \cdot 10^{-6}$ cm^{-1}ohm^{-1}, molar conductance $\lambda = 0.825$ cm^{-1}ohm^{-1}.

Complex Compound formed by 5,10-Disodio-5,10-dihydrophenazine with Diethyl Ether

A mixture of 4.5 g of N-(diphenylmethylene)aniline, 1.1 g of sodium, and 80 ml of ether was shaken for 50 hours. The cherry-red solution of the disodium derivative of N-(diphenylmethylene) aniline was filtered, and a solution of 0.6 g of phenazine in 50 ml of ether was added. The resulting precipitate was filtered off, washed with ether, dried to constant weight, and analyzed as described above.

Found %: 16.0; 15.9; phenazine 62.20; 61.30



$2Na \cdot (C_2H_5)_2O$. Calculated %: Na 15.3; phenazine 60.0

SUMMARY

1. Dimetal compounds of phenazine prepared in a medium of 1,2-dimethoxyethane are complex compounds. The disodium compound contains two molecules of 1,2-dimethoxyethane, and the dilithium compound contains six molecules of 1,2-dimethoxyethane.

2. In 1,2-dimethoxyethane solution, dimetal compounds of phenazine conduct electricity and have an ionic structure. In these compounds, one alkali-metal atom forms part of a complex cation, and the other is covalently bound to the negatively charged phenazine molecule.

3. The disodium compound of phenazine prepared in ether by the action of the disodium derivative of N-(diphenylmethylene)aniline on phenazine is a complex compound, each molecule of which contains one molecule of ether.

Received October 26, 1954

N. D. Zelinsky Institute of Organic
Chemistry of the USSR Academy of
Sciences

LITERATURE CITED

[1] B. M. Mikhailov and A. N. Blokhina, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1950, No. 3, 304.

[2] B. M. Mikhailov and N. G. Chernova, Proc. Acad. Sci. USSR, 74, 939 (1950).

[3] W. Schlenk, E. Bergmann, Ann. 463, 300 (1928).

[4] B. M. Mikhailov and N. G. Chernova, Proc. Acad. Sci. USSR, 78, 489 (1951).

BLANK
PAGE

CATALYTIC HYDROGENATION OF DOUBLY UNSATURATED COMPOUNDS HAVING A CONJUGATED SYSTEM OF DOUBLE BONDS

COMMUNICATION 3. HYDROGENATION OF 2,3-DIMETHYL-1,3-BUTADIENE IN PRESENCE OF PLATINUM, NICKEL, AND PALLADIUM

I. V. Gostunskaya, G. V. Loza, and B. A. Kazansky

The present work forms a continuation of our investigations into the laws governing the addition of a catalytically activated hydrocarbon to a conjugated diene hydrocarbon in presence of platinum, palladium, and nickel. A paper by Kazansky and Popova [1] describes the reduction of biisocrotyl (2,5-dimethyl-2,4-hexadiene) — a hydrocarbon in which methyl groups are attached to the first and fourth carbon atoms of the conjugated system. Hydrogen added mainly at the 1,2-positions of the conjugated system. The content of 2,5-dimethyl-3-hexene — the hydrocarbon formed by 1,4-addition — was 13%, 6%, or 9% for hydrogen over platinum, palladium, or nickel, respectively.

In the hydrogenation of isoprene [2] — a diene hydrocarbon in which there is a methyl group on the second atom of the conjugated system — the character of the addition of hydrogen, while not greatly different in the case of platinum, is greatly changed in the case of nickel and palladium: the contents of 2-methyl-2-butene — the product of 1,4-addition of hydrogen — are 15% for platinum, 41% for palladium, and 40% for nickel.

The present work was undertaken with the object of elucidating the effect of two methyl groups on the second and third atoms of the conjugated system, the hydrocarbon examined being 2,3-dimethyl-1,3-butadiene. The catalytic hydrogenation of this hydrocarbon has been studied by Lebedev [3] and by Dupont [4]. According to Lebedev's results, when one molecule of hydrogen adds to 2,3-dimethyl-1,3-butadiene in presence of platinum, a mixture of hydrocarbons of the following composition is obtained:

2,3-Dimethyl-1-butene	—	32 mole %
2,3-Dimethyl-2-butene	—	12 mole %
2,3-Dimethylbutane	—	28 mole %
2,3-Dimethyl-1,3-butadiene	—	28 mole %

The authors did not isolate individual hydrocarbons from the hydrogenation product, but derived their information from kinetic hydrogenation curves obtained after removal of unchanged diene.

Dupont studied the hydrogenation of 2,3-dimethyl-1,3-butadiene in presence of Raney nickel, and he analyzed the hydrogenation products by the Raman spectrum method. The contents of 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene in the hydrogenation products were 63% and 37%, respectively.

In the present work we have investigated the catalytic hydrogenation of 2,3-dimethyl-1,3-butadiene in presence of platinum black, of palladium black, and of Raney nickel. The composition of the hydrogenation products was determined by the method employed in the previous investigations on biisocrotyl and isoprene, namely, by rectification of the reaction mixture through highly efficient columns and investigation of the composition of the fractions obtained (by determinations of refractive index, density, and bromine numbers). The use of the same method of investigation for different dienes in presence of different catalysts makes the results comparable and makes it possible to establish the effect of the structures of the original dienes and of the identity of the catalyst on the direction of addition of hydrogen.

Our study of the hydrogenation of 2,3-dimethyl-1,3-butadiene shows that, as in the case of the hydrogenation of isoprene and biisocrotyl, addition proceeds in all possible directions. The content of 2,3-dimethyl-2-butene — the 1,3-addition product — in the reaction mixture is 13 mole % for hydrogenation over platinum and 25 mole % for hydrogenation over nickel. In hydrogenation over platinum — as in all such cases studied by Lebedev and by us — addition of one molecular proportion of hydrogen results in the formation not only of monoolefins, but also of the fully hydrogenated product, some of the diene, therefore, remaining unchanged.

Comparison of the results for 2,3-dimethyl-1,3-butadiene and isoprene shows that the difference in the compositions of the reaction mixtures is inappreciable when platinum is used as catalyst, but the change is much greater when nickel is used, the proportion of 1,4-addition product being lower in the dimethylbutadiene hydrogenation products than in the isoprene hydrogenation products.

EXPERIMENTAL

Synthesis and Properties of 2,3-Dimethyl-1,3-butadiene. 2,3-Dimethyl-1,3-butadiene was prepared by the dehydration of pinacol, which was synthesized by Adams' method, as modified by Getling and Zhdanova [5]. The dehydration of pinacol was carried out by Lebedev's method [3], in which it is treated with phosphoric acid in acetic anhydride; this method gives a higher yield of the diene than any other method reported. The synthesized diene had the following constants: b.p. 69° (742 mm); n_D^{20} 1.4393; d_4^{20} 0.7266; found MR_D 29.70, calculated MR_D for $C_6H_{10}(F_2)$ 28.97. The literature [6] gives b.p. 68.9° (760 mm); n_D^{20} 1.4390; d_4^{20} 0.7263.

Hydrogenation Procedure and Investigation of the Hydrogenation Products. The hydrogenation of 2,3-dimethyl-1,3-butadiene was carried out at room temperature and under atmospheric pressure in a hydrogenation flask, which was shaken at the rate of 300 double shakes per minute. The amount of hydrogen adsorbed was measured in a 180 ml gas buret having 0.2 ml graduations. Readings for the plotting of the hydrogenation curve were taken every 30 seconds. The platinum and palladium blacks were prepared by Willstätter's method [7], and Raney nickel was prepared by Adkins' method [8]. The solvent used was 96% ethanol.

In the experiments on the composition of the products of the addition of one molecular proportion of hydrogen to the diene, reaction was allowed to proceed until the volume of hydrogen calculated for the given weight of diene had been absorbed. Distillation through a column yielded an azeotropic mixture of the hydrogenation products and alcohol, from which the alcohol was removed by washes with saturated calcium chloride solution. The hydrocarbon mixture was then distilled over sodium. In order to remove the unchanged diene present when the hydrogenation was carried out over platinum, the mixture of hydrocarbons was refluxed with maleic anhydride for one hour. The hydrocarbons obtained were identified by determining the boiling points, densities, refractive indices, and bromine numbers of the fractions [9]. The calculation of the amounts of the various hydrocarbons formed in the hydrogenation process was carried out on the basis of data from the fractionation curves and of the properties of the fractions.

Hydrogenation of 2,3-Dimethyl-1,3-butadiene in Presence of Platinum Black. In Table 1, we give the conditions under which two experiments on the hydrogenation of 2,3-dimethyl-1,3-butadiene were carried out with the object of determining the hydrogenation curves.

TABLE 1

Expt. No.	Amount of hydrocarbon (g)	Amount of catalyst (g)	Amount of alcohol (ml)	Temperature (°C at 740 mm)	Amount of hydrogen (ml)	
					absorbed	calculated
1	0.4083	0.0972	10.0	22	220	242
2	0.4097	0.0978	10.0	22	256	249

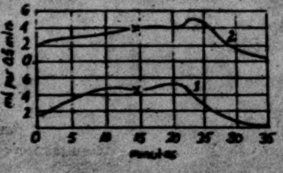


Fig. 1. Curve for the hydrogenation of 2,3-dimethyl-1,3-butadiene in presence of platinum black: 1) Experiment 1; 2) Experiment 2.

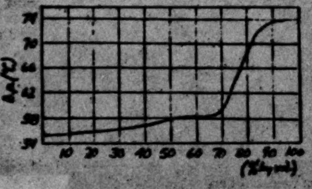


Fig. 2. Fractionation curve of the products of the addition of one molecular proportion of hydrogen to 2,3-dimethyl-1,3-butadiene in presence of platinum black.

The hydrogenation curve, which is given in Fig. 1, shows that in presence of platinum the hydrogenation process is complicated. The addition of one molecular proportion of hydrogen (the point at which this occurs is indicated on the curve by the sign $^{\times}$) is not associated with any feature of the curve; a change in the rate of hydrogenation occurs when about 70% of the calculated amount of hydrogen has added. Our hydrogenation curves are very similar to those obtained by Lebedev.

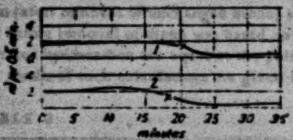


Fig. 3. Curve for the hydrogenation of 2,3-dimethyl-1,3-butadiene in presence of Raney nickel: 1) Experiment 1; 2) Experiment 2.

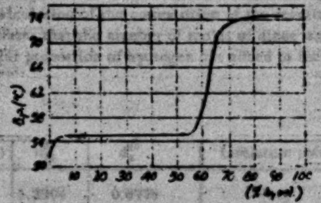


Fig. 4. Fractionation curve of the products of the addition of one molecular proportion of hydrogen to 2,3-dimethyl-1,3-butadiene in presence of Raney nickel.

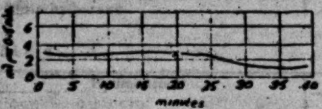


Fig. 5. Curve for the hydrogenation of 2,3-dimethyl-1,3-butadiene in presence of palladium black.

With the object of studying the hydrogenation of 2,3-dimethyl-1,3-butadiene in greater detail, we carried out the 50% hydrogenation of 54.0 g of diene, i.e. the addition of one mole of hydrogen to one mole of diene. From the mixture with alcohol, 47.0 g of hydrogenation product was isolated, and the treatment of this with maleic anhydride yielded 32 g of a hydrocarbon mixture, which was then distilled through a 70-plate column. The results of the fractionation and the characteristics of the fractions obtained are given in Table 2; the fractionation curve is given in Fig. 2.

TABLE 2

Fraction No.	B.p. (°C at 760 mm)	Amount of fraction (% by weight)	n_D^{20}	d_4^{20}	MR Calculated	MR Found	Bromine number	Amount of olefins (%)	Amount of parafin (%)
I	55.3-56.1	36.2	1.3882	0.6771	29.44 for C_6H_{12}	29.29	186.1	97.6	2.4
II	56.1-57.8	18.2	1.3822	0.6707	–	–	115.0	60.3	39.7
III	57.8-58.3	15.6	1.3741	0.6621	29.90 for C_6H_{14}	29.67	5.0	2.6	97.4
IV	58.3-72.2	10.9	1.4030	0.6940	–	–	96.2	50.5	49.5
V	72.2-73.5	7.5	1.4162	0.7112	29.44 for C_6H_{12}	29.39	*	–	–
Residue in still		3.8							
Total		92.2%							
Losses		7.8%							

---

* Agreeing results could not be obtained in the determination of the bromine number of Fraction V, which consisted mainly of 2,3-dimethyl-2-butene.

The constants of the hydrocarbons that could be formed by the hydrogenation of 2,3-dimethyl-1,3-butadiene are given in Table 3.

A comparison of the characteristics of the fractions with the data in Table 3 shows that Fraction I contains mainly 2,3-dimethyl-1-butene, Fraction III mainly 2,3-dimethylbutane, and Fraction V mainly 2,3-dimethyl-2-butene, probably with some unremoved diene as impurity, which raises the constants of Fraction V somewhat, as compared with those of the pure monoolefin; Fractions II and IV are intermediate fractions containing the saturated hydrocarbon in admixture with monoolefins, i.e. with 2,3-dimethyl-1-butene (Fraction II) and with 2,3-dimethyl-2-butene (Fraction IV). The compositions of the mixtures were determined with the aid of their bromine numbers. On the basis of the data in Table 2, the total contents of the various hydrocarbons in the mixture taken for fractionation (after removal of unchanged diene) were calculated. The calculation of the composition of the reaction mixture before removal of diene was based on Lebedev's rule, which states that the number of moles of diene and of saturated hydrocarbon are equal at the point at which one molecular proportion of hydrogen has added to the diene. The results of such calculations are given in Table 4.

TABLE 3

Hydrocarbon	B.p. (°C at 760 mm)	n_D^{20}	d_4^{20}	Literature reference
2,3-Dimethyl-1-butene	55.64	1.3904	0.6779	[10]
2,3-Dimethyl-2-butene	73.21	1.4122	0.7080	[10]
2,3-Dimethylbutane	57.99	1.3750	0.6616	[10]

TABLE 4

Hydrocarbon	Amount	
	After removal of diene (mole %)	Before removal of diene (mole %)
2,3-Dimethyl-1-butene	51.5	39
2,3-Dimethyl-2-butene	17.1	13
2,3-Dimethylbutane	31.4	24
2,3-Dimethyl-1,3-butadiene	–	24

TABLE 5

Expt. No.	Amount of hydrocarbon (g)	Amount of catalyst (g)	Amount of alcohol (ml)	Temperature (°C at 754 mm)	Amount of hydrogen (ml)	
					absorbed	calculated
1	0.3229	0.1151	25.0	18	108.0*	194
2	0.3344	0.1197	25.0	18	101.4*	199

---

* In view of the fact that, in its last stage, hydrogenation went with a very low, though constant velocity, the reaction was not carried out to completion.

TABLE 6

Fraction No.	B.p. (°C at 760 mm)	Amount of fraction (% by weight)	n_D^{20}	d_4^{20}	MR		Bromine number	Amount of olefins (%)
					Calculated	Found		
I	50–55.5	2.4	1.3879	–	for C_6H_{12}			
II	55.5	57.1	1.3903	0.6776	29.44	29.38	190	100
III	55.6–70.4	6.2	1.4250	0.7200	–	–	–	–
IV	70.5–73.9	16.5	1.4173	0.7185	–	–	–	–
V	73.9	10.2	1.4120	0.7114	29.44	29.38	*	–
Residue in still and losses		7.6						

---

* It was not found possible to determine the bromine number.

The predominating direction of the hydrogenation of 2,3-dimethyl-1,3-butadiene in presence of platinum black is addition of hydrogen at the 1,2-positions of the conjugated system. Our results are close to those of Lebedev.

Hydrogenation of 2,3-Dimethyl-1,3-butadiene in Presence of Raney Nickel. In Table 5 we give the conditions under which two experiments on the hydrogenation of 2,3-dimethyl-1,3-butadiene were carried out with the object of determining the hydrogenation curves. The hydrogenation curves are given in Fig. 3.

The hydrogenation curves for a nickel catalyst are greatly different from those for the platinum catalyst. The marked breaks in the curves occur at the points corresponding to the addition of one molecular proportion of hydrogen.

In order to study the products of reaction in presence of Raney nickel, the 50% hydrogenation of 51 g of 2,3-dimethyl-1,3-butadiene was carried out. From the mixture with alcohol, 44 g of hydrogenation products was isolated and were distilled in presence of hexane through a 70-plate column. The fractionation curves are given in Fig. 4. The results of the fractionation and the characteristics of the fractions obtained are given in Table 6.

Fractions I and II contain mainly 2,3-dimethyl-1-butene, Fraction III contains a mixture of 2,3-dimethyl-1-butene and uncharged diene, Fraction IV 2,3-dimethyl-2-butene with a little diene impurity, and Fraction V 2,3-dimethyl-2-butene. No completely hydrogenated product was found. On the basis of the fractionation curve and the data of Table 6, an approximate calculation was made of the composition of the mixture of hydrocarbons obtained in the hydrogenation:

2,3-Dimethyl-1-butene — 26.8 g (66.6 mole %)
2,3-Dimethyl-2-butene — 10.4 g (25.1 mole %)
2,3-Dimethyl-1,3-butadiene — 3.4 g (8.3 mole %)

As in hydrogenation over platinum, in presence of nickel the main direction of the reaction is addition of hydrogen at the 1,2-positions of the conjugated system.

Hydrogenation of 2,3-Dimethyl-1,3-butadiene in Presence of Palladium Black. One experiment was carried out for the purpose of determining the kinetic curve. The amounts taken were 0.4950 g (0.006 mole) of diene and 0.0635 g (0.0006 mole) of catalyst. The diene was dissolved in 10 ml of ethanol. The hydrogenation was carried out at 21° and 750 mm. The amount of hydrogen absorbed in the hydrogenation of the diene was 261 ml, the amount required theoretically being 293 ml. The hydrogenation curve, which is given in Fig. 5, is close to that for the nickel catalyst. Unfortunately, we were unable to carry out the 50% hydrogenation of larger amounts of 2,3-dimethyl-1,3-butadiene in presence of palladium black.

SUMMARY

1. In presence of platinum or nickel, the hydrogenation of 2,3-dimethyl-1,3-butadiene proceeds in all possible directions.

2. Comparison of the results for the hydrogenation of 2,3-dimethyl-1,3-butadiene and of isoprene shows that, in presence of platinum, the relative extents of the addition of hydrogen in the various directions are approximately the same for both dienes, whereas in presence of nickel they are different.

3. In the hydrogenation of 2,3-dimethyl-1,3-butadiene in the presence of nickel, the amount of 1,4-addition product (25%) is less than in the hydrogenation of isoprene under similar conditions (40%).

LITERATURE CITED

[1] B. A. Kazansky and N. I. Popova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1952, No. 3, 422 (T. p. 427)*.

[2] B. A. Kazansky, I. V. Gostunskaya, and A. M. Granat, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, No. 4, 670 (T. p. 601)*.

[3] S. V. Lebedev and A. I. Yakubchik, J. Russ. Chem. Soc., 60, 793 (1928).

[4] J. Dupont, C. Paquot, Comptes rend., 205, 805 (1937).

[5] V. A. Getling and N. V. Zhdanova, Synth. Rubber, 5, 15 (1933).

[6] R. M. Doss, Physical Constants of the Principal Hydrocarbons, 1943.

[7] R. Willstätter, Ber., 41, 2198 (1908).

[8] H. A. Adkins, V. Covert, J. Am. Chem. Soc., 51, 4116 (1932).

---

* T.p. = C. B. Translation pagination.

[9] G. D. Galpern and E. V. Vinogradova, Chemistry of Solid Fuel, 8, 354 (1937).

[10] R. D. Obolentsev, Physical Constants of the Hydrocarbons of Liquid Fuels and Oils, State Fuel Tech. Press, Moscow, 1953.

Received October 7, 1954

M. V. Lomonosov State
University, Moscow

CATALYTIC DEHYDROCYCLIZATION OF PIPERYLENE

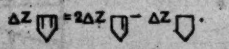
N. I. Shuikin and V. A. Tulupov

There have been only a few isolated investigations on the contact-catalysis reactions of piperylene. Thus, Frank, Emmick, and Johnson [1] studied the thermal interconversion of the cis-and trans-isomers of piperylene at 600° and also the iodine-catalyzed interconversion of the isomers at the boiling point of the diene. They found that each of the pure piperylene isomers yields a mixture of cis - and trans-forms. At 600°, this mixture contains 40-45% of cis-piperylene, and at the boiling point in presence of iodine the equilibrium mixture, obtained after an 18-hour treatment, contains 87% of the trans-form.

Kennedy and Hetzel [2] investigated the catalytic reactions of piperylene in presence of $Al_2O_3 + Cr_2O_3$ and of aluminosilicates of various compositions. They observed that, in a vacuum at 600-620°, piperylene undergoes partial cracking with simultaneous formation of cyclopentadiene in a yield that, in some experiments, amounted to as much as 9% of the condensate. These authors consider that the cyclization reaction of piperylene is noncatalytic. It appeared to us that this conclusion was not sufficiently well grounded, and we therefore decided to make a more detailed study of the reaction. We have therefore investigated the reactions of piperylene at various temperatures and pressures in presence of various catalysts, and we have tried to determine the effect of the relative amounts of cis and trans isomers in the original piperylene on the yield of cyclopentadiene. At the same time we have observed the interconversion of cis- and trans-piperylenes under the action of the catalyst. From thermodynamic data for piperylene, as given by Kilpatrick, Beckett, Prosen, Pitzer, and Rossini [3], with the help of the approximate equation

$$-RT \ln K_p = \Delta H^\circ_{298.16^\circ} - T\Delta S^\circ_{298.16^\circ} = \Delta Z,$$

we calculated, on the one hand, the equilibrium constant for the interconversion of cis- and trans-piperylenes at their boiling points, and on the other hand, the logarithms of the cyclization-reaction constants for various temperatures. As no values of the thermodynamic potential were available for cyclopentadiene, we calculated these quantities from the corresponding quantities for cyclopentane and cyclopentene [4], neglecting the effect of the conjugation of the double bonds in cyclopentadiene and assuming that



For the interconversion of the geometric isomers of piperylene we took ΔZ to be 35,816 and 36,025 cal/mole for the cis-and trans-forms respectively, and found that $K_{p\,315.16^\circ} = 1.004$, corresponding to contents of 50.01% of cis- and 49.99% of trans-piperylene in the mixture. In view of the fact that, with rise in temperature right up to 1500° K, the difference in the values of ΔZ for the piperylene isomers remains almost constant — not more than 200-300 cal/mole — the equilibrium constant tends to the value of unity. It follows that, at almost all temperatures, the equilibrium mixture should contain equal amounts of the two forms, and not greatly differing amounts as found by Frank and coworkers, who give the values: 87% of trans-form at 315.16° K and 55-60% at 873.16° K [1]. The temperature dependence of the logarithm of the equilibrium constant for the formation of cyclopentadiene is shown in Fig. 1.

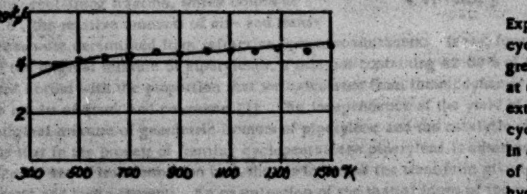


Fig. 1. Temperature dependence of the logarithm of the equilibrium constant for the formation of cyclopentadiene from piperylene.

As can be seen from Table 1 (see Experimental), whereas the yields of cyclopentadiene in the catalyzate vary greatly with temperature, attaining 50.4% at 650° over $Al_2O_3 + MnO$ (1 : 2), the actual extent of conversion of piperylene into cyclopentadiene does not exceed 18.5%. In a study of the kinetics of the cyclization of piperylene we established that the dehydrocyclization reaction is extremely slow. The rate constants of the reaction determined at 550° and 600° are $8.03 \cdot 10^{-5}$

and $5.41 \cdot 10^{-4}$ mole/cm, respectively. The activation energy is 59,105 cal/mole. With these values for the constants, the complete conversion of one mole of piperylene into cyclopentadiene at 600° in one hour will require a layer of catalyst about $1.8 \cdot 10^{5}$ cm in length and of unit cross section; alternatively, if the layer is of unit length the time required will be about the same. . It would appear that the obstacle to the attainment of thermodynamic equilibrium is the low rate of reaction, so that it should be possible to attain a greater degree of conversion by increase in the time of contact between piperylene and catalyst. However, as will be seen from the kinetic results represented in Fig. 2, the rate of formation of cyclopentadiene does not depend on the time of contact between piperylene and catalyst.

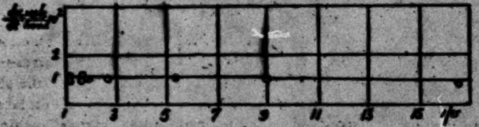


Fig. 2. Dependence of the rate of formation of cyclopentadiene from piperylene on the reciprocal of the space velocity

It follows from the data in Table 1 that, contrary to Kennedy and Hetzel's assertion [2], the yield of cyclopentadiene is dependent on the nature of the catalyst, so that the reaction is a catalytic one. This is particularly clear from the results of experiments with alumina-manganese oxide catalysts of various compositions. Whereas the yield of cyclopentadiene is greatly affected by the nature and composition of the catalyst, the extent of the conversion of piperylene into cyclopentadiene does not depend on the relative proportions of cis- and trans-forms present in the original piperylene, as can be seen from the data in Table 6.

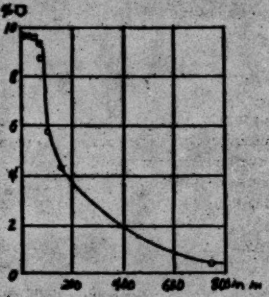


Fig. 3. Dependence of the yield of cyclopentadiene on pressure for the catalyst $Al_2O_3 + Cr_2O_3$ (1 : 1).

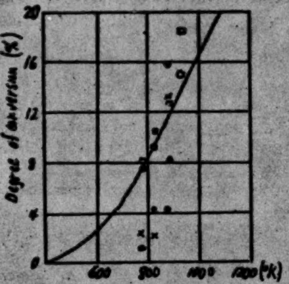
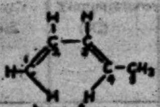
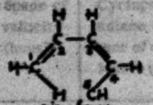


Fig. 4. Temperature dependence of the degree of conversion of piperylene into 1,4-pentadiene (calculated curve) and into cyclopentadiene [points corresponding to values obtained with the following catalysts: o) Zn_2SiO_4; □) Al_2O_3 + MnO (1 : 2); Δ) $Al_2O_3 + Cr_2O_3$ (1 : 1); X) – Pt-aluminosilicate; •, Pt–SiO_2].

In one series of experiments (Table 7), the catalyzates, after removal of cyclopentadiene, were fractionated through a 30-plate column. In the piperylene-containing fraction, which boiled at 41.7-43.8°, the relative amounts of cis- and trans-piperylenes were determined from refractive index measurements. It was found that, irrespective of the composition of the original mixture of piperylenes, a mixture containing 42-50% of trans-piperylene was obtained, which is in close accord with the proportion that we calculated from thermodynamic data and is somewhat at variance with the results of Frank and coworkers [1]. The independence of the yield of cyclopentadiene on the composition of the original mixture of geometric isomers of piperylene and the catalytic character of the reaction enable us to conclude that in the process of forming cyclopentadiene piperylene is adsorbed on the catalyst in such a way that in the further act of transformation both the cis-form and the trans-form give intermediate states that are equivalent in energetic and steric respects. An examination of the spatial forms of the two isomers indicates that the molecule is most probably adsorbed at the 3-4 position.



trans-form



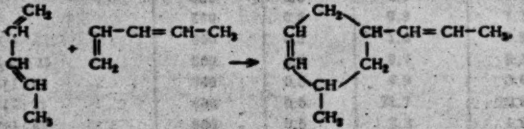
cis-form

The interconversion of the two geometric forms is possible only when rotation around the 3-4 bond can occur; the removal of the high restraining potential barrier occurs as a result of the weakening or opening of the π-bond and the attachment of the piperylene to the catalyst at position 4.

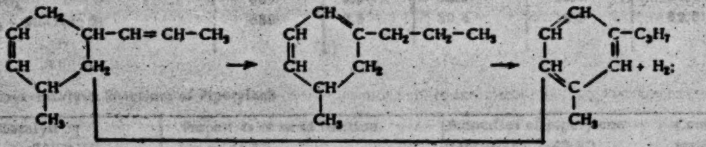
The pressure at which the reaction is carried out has a substantial effect on the yield of cyclopentadiene. As can be seen from the curve of Fig. 3 (plotted from the data in Table 7), at comparatively low pressures — up to about 70 mm — the yield of cyclopentadiene remains almost unchanged. With increase of pressure, however, the yield falls sharply, and at the same time the amount of cracking increases.

In experiments at atmospheric pressure, we isolated benzene, toluene, and o-xylene from the catalysts products. We consider that these hydrocarbons are formed as a result of secondary transformations of dimerization products of piperylene.

As shown earlier [5], piperylene dimerizes into 3-methyl-5-propenylcyclohexene:



which may then udergo dehydrogenation — either directly, or after isomerization into methylpropylcyclohexadiene — with formation of propyltoluene:



which, as a result of dealkylation and isomerization, probably yields the aromatic hydrocarbons that we found in the catalyzate. It must be noted that the cyclization of piperylene to cyclopentadiene is a complex process, which is accompanied by hydrogen-redistribution reactions, isomerization, polymerization, and cracking.

EXPERIMENTAL

Preparation of Catalysts

Pure and Mixed Oxide Catalysts [$Al_2O_3 + Cr_2O_3$ (1 : 1); Al_2O_3 + MnO (1 : 1, 1 : 2, 1 : 4, 1 : 6); Al_2O_3, ZnO] were prepared from the corresponding nitrates by precipitation with 25% ammonia solution. They were washed free from nitrate, formed into cylinders, and dried at 150°. The alumina-manganese oxide catalysts were reduced, before being used in the experiments, by treatment with hydrogen in the catalysis tube with gradual increase in temperature to 600°, and then until water ceased to separate.

Zinc and Magnesium Silicates (Zn_2SiO_4, Mg_2SiO_4) were prepared by grinding separately prepared zinc and magnesium hydroxides with silica gel in a mortar. After the mixing, the catalysts were formed into cylinders and dried at 150°. Andalusite was ground mechanically into small particles and used without preliminary treatment.

TABLE 1

Cyclization of Piperylene to Cyclopentadiene at 25-30 mm

Expt. No.	Catalyst	Temperature (°C)	Space of velocity (hour^{-1})	Cyclopentadiene content of catalyzate (%)	Extent of conversion into cyclopentadiene (%)	Extent of cracking (%)
1	Pt−SiO_2	500	0.5	1.3	1.1	12.0
2	Pt−aluminosilicate	500	0.006	2.0	2.2	33.0
3	Zn_2SiO_4	500	0.4	8.6	7.5	13.1
4	Al_2O_3 + MnO (1 : 2)	500	0.5	9.1	8.1	12.2
5	Pt−SiO_2	550	0.5	5.3	4.1	22.5
6	Pt−aluminosilicate	550	0.16	2.3	2.0	16.0
7	Zn_2SiO_4	550	0.5	10.2	9.1	12.7
8	Al_2O_3 + MnO (1 : 2)	550	0.5	12.1	10.5	13.0
9	Al_2O_3 + MnO (1 : 4)	550	0.5	1.1	0.9	13.5
10	Pt−SiO_2	600	0.5	5.4	4.1	25.0
11	Pt−aluminosilicate	600	0.2	23.0	13.1	24.0
12	Pd−charcoal	600	0.5	10.7	7.3	32.0
13	Active charcoal	600	0.5	6.5	5.6	18.0
14	Zn_2SiO_4	600	0.5	21.9	15.9	15.0
15	ZnO	600	0.5	0.6	0.2	34.5
16	Mg_2SiO_4	600	0.5	9.9	7.1	28.0
17	Al_2O_3	600	0.5	1.4	0.9	37.0
18	Al_2O_3 + Cr_2O_3 (1 : 1)	600	0.5	9.7	8.1	15.4
19	Al_2O_3 + MnO (1 : 1)	600	0.5	6.9	3.6	54.5
20	Al_2O_3 + MnO (1 : 2)	600	0.5	21.7	12.8	43.7
21	Al_2O_3 + MnO (1 : 4)	600	0.5	2.3	1.6	32.0
22	Al_2O_3 + MnO (1 : 6)	600	0.5	4.6	2.5	21.0
23	Al_2O_3 + TiO_2 (1 : 19)	600	0.5	3.5	2.0	12.5
24	Andalusite	600	0.5	5.9	5.4	10.0
25	Zn_2SiO_4	650	0.5	32.9	15.0	54.4
26	Al_2O_3 + MnO (1 : 2)	650	0.5	50.4	18.5	62.0

TABLE 2

Products of Contact-catalysis Reactions of Piperylene

Expt. No. *	Catalyst	Properties of head fraction (up to 41.7°)				Properties of piperylene fraction (41.7-43.8°)			Content of residue (%) by volume
		B.p. (°C, corrected)	d_4^{20}	n_D^{20}	Content (% by volume)	d_4^{20}	n_D^{20}	Content (%) by volume)	
1, 5 and 10	Pt−SiO_2	26-41.7	0.6628	1.3983	17.3	0.6821	1.4275	67.9	13.4
2, 6 and 11	Pt−aluminosilicate	27.5-41.7	0.6701	1.4010	10.7	0.6829	1.4331	75.3	8.7
12	Pd−charcoal	18-41.7	0.6680	1.3955	15.5	0.6834	1.4329	73.5	11.1
13	Active charcoal	22-41.7	0.6674	1.3947	14.2	0.6831	1.4330	80.2	5.4
3, 7, 14 and 25	Zn_2SiO_4	34.3-41.7	0.6915	1.4122	5.9	0.6828	1.4330	75.4	17.7
19	Al_2O_3 + MnO (1 : 1)	30-41.7	0.6884	1.4085	4.8	0.6830	1.4330	84.4	8.9
4, 8, 20 and 26	Al_2O_3 + MnO (1 : 2)	27.0-41.7	0.6718	1.4015	7.4	0.6829	1.4331	81.7	10.3
9 and 21	Al_2O_3 + MnO (1 : 4)	26.3-41.7	0.6640	1.3975	12.9	0.6824	1.4325	76.7	9.0
22	Al_2O_3 + MnO (1 : 8)	26.0-41.7	0.6615	1.3960	16.0	0.6825	1.4325	73.0	9.7
18	Al_2O_3 + Cr_2O_3 (1 : 1)	26.0-41.7	0.6630	1.3970	20.1	0.6828	1.4325	77.1	12.5
23	Al_2O_3 + TiO_2 (1 : 19)	26.5-41.7	0.6693	1.3992	14.7	0.6836	1.4339	73.1	11.8
16	Mg_2SiO_4	29-41.7	0.6720	1.4031	8.4	0.6812	1.4307	72.1	18.2
24	Andalusite	27.3-41.7	0.6712	1.3997	4.3	0.6828	1.4332	88.2	5.9
17	Al_2O_3	29.4-41.7	0.6883	1.4075	4.7	0.6824	1.4329	85.9	8.3
15	ZnO	30.1-41.7	0.6892	1.4080	6.2	0.6817	1.4328	84.7	7.9

---

* The numbering is the same as in Table 1.

TABLE 3

Products Isolated after the Bromination of the Head Fractions (B.p. up to 41.7°)

Expt. No.	Paraffin part				Solid bromo compounds	
	B.p. (°C, corrected)	d_4^{20}	n_D^{20}	Volume (ml)	I (m.p. in °C)	II (m.p. in °C)
1, 5 and 10	27.3-36.5	0.6270	1.3581	2.3	84.6	116
2, 6 and 11	27.5-37.1	0.6283	1.3585	1.2	86.3-86.5	116
3, 7, 14 and 25	none present				–	116
4, 8, 20 and 26	27.2-37.4	0.6266	1.3579	1.3	–	116

TABLE 4

Liquid Bromo Compounds Isolated from the Products of the Bromination of the Head Fractions (B.p. up to 41.7°) of the Catalyzates from Experiments 1, 2, 5, and 7

B.p. of fraction / Expt. No.	55-60° (12 mm)		60-65° (12 mm)		65-70° (12mm)		Above 70° (mm)
	d_4^{20}	n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}	n_D^{20}	n_D^{20}
1	1.6712	1.5101	1.6772	1.5093	1.6752	1.5112	1.5135
2	1.6710	1.5092	1.6781	1.5107	1.6760	1.5107	1.5140
5	1.6707	1.5090	1.6780	1.5105	1.6759	1.5110	1.5137
7	1.6715	1.5098	1.6782	1.5110	1.6762	1.5106	1.5160

TABLE 5

Data from the Literature for the Properties of Dibromopentanes

Dibromopentane	B.p. (°C)	d_4^{20}	n_D^{20}	Literature reference
2,3-Dibromo-2-methylpentane	56-58 (12)	1.6717	1.5112	[7]
1,2-Dibromopentane	58-60 (10-11)	1.6708	1.5088	[8]
2,3-Dibromo-4-methylpentane	65-66 (12)	–	–	[9]
2,3-Dibromopentane	58-58.5 (12)	1.6821	1.5099	Determined by us

TABLE 6

Catalytic Transformations of Various Mixtures of cis- and trans-Piperylenes (Space Velocity 0.5 hour^{-1})

Expt. No.	Catalyst	Original piperylene		Cyclopentadiene content of catalyzate (%)	Piperylene isolated from catalyzate	
		n_D^{20}	Content of trans form (%)		n_D^{20}	Content of trans form (%)
1	Al_2O_3 + MnO (1 : 2)	1.4310	83.3	20.4	1.4332	46.7
2	Al_2O_3 + MnO (1 : 2)	1.4330	50.0	21.7	1.4335	41.7
3	Zn_2SiO_4	1.4325	57.0	21.9	1.4330	50.0
4	Zn_2SiO_4	1.4344	27.0	21.0	1.4333	45.0

Finely Dispersed Platinum and Palladium on Carriers were prepared from palladous and platinic chlorides, in the form of solutions absorbed in activated charcoal and commercial aluminosilicate catalyst, by reduction in the cold with formalin and alkali. These catalysts contained 5% Pd (on charcoal) and 6_1 Pt (on aluminosilicate).

Platinum on Silica Gel was prepared by the calcination of 150 ml of silica gel impregnated with a solution of 7 g of platinic chloride in 50 ml of water, with subsequent reduction with hydrogen at 300°. The catalyst contained 4% Pt.

Apparatus, Experimental Procedure, and Analysis of Catalyzates

Experiments on the reactions of piperylene were carried out in a quartz tube, 18 mm in diameter, in a continuous-flow system. The temperature was measured with a chromel-alumel thermocouple. In a normal experiment, piperylene was passed to the reaction zone from an automatic buret, and in the kinetic measurements the supply was effected with the aid of a cylinder of about 100 ml capacity which we constructed; this was attached to the catalysis tube by a ground joint. The cylinder contained a spiral heated by an electric current supplied from a stabilized source of potential difference. The rate of supply of material was determined from the value of the current passing through the spiral. For each experiment, 20-80 g of piperylene was taken. All of the experiments, except one, were carried out in a vacuum. The reaction products were collected in a receiver cooled with water and in a series of three traps, two of which were immersed in a mixture of dry ice and methanol, and the third in liquid nitrogen. The gases that condensed in the last trap were mainly C_2-C_4 unsaturated hydrocarbons and methane. Immediately after the experiment, the liquid catalyzate was analyzed for cyclopentadiene by Afanasyev's method [6]. The results of the experiments are given in Table 1.

TABLE 7

Dependence of the Yield of Cyclopentadiene on Pressure in the Reactions of Piperylene over $Al_2O_3 + Cr_2O_3$ (1 : 1)

Expt. No.	Pressure (mm)	Cyclopentadiene content of catalyzate (%)	Residue (B.p. > 44°)		Extent of cracking (%)
			Weight (g)	Fraction of catalyzate (%)	
1	10	9.7	3.7	10.1	15.4
2	30	9.7	3.7	10.5	17.8
3	50	9.6	3.9	12.1	36.5
4	70	9.4	4.0	13.5	37.4
5	90	8.9	4.2	13.8	38.0
6	100	5.7	4.2	14.1	39.0
7	150	4.3	4.5	14.3	43.7
8	760	0.4	4.7	14.0	57.5

TABLE 8

Dependence of the Yield of Cyclopentadiene on the Time of Contact with Platinum-Aluminosilicate Catalyst

Expt. No.	Temperature °C	Supply of piperylene (mole/hour)	Rate of formation of cyclopentadiene (mole/hour)	Degree of conversion (as a fraction)	Rate constant (mole/cm)
1	600	0.910	0.0099	0.022	0.000500
2	600	0.667	0.0120	0.037	0.000601
3	600	0.576	0.0107	0.040	0.000577
4	600	0.397	0.0100	0.052	0.000501
5	600	0.197	0.0107	0.102	0.000500
6	600	0.910	0.0110	0.024	0.000545
7	600	0.667	0.0107	0.034	0.000567
8	550	0.164	0.0031	0.019	0.0000777
9	550	0.197	0.0035	0.016	0.0000812
10	550	0.164	0.0033	0.020	0.0000820

After cyclopentadiene had been determined, the catalyzates were distilled over sodium hydrogen sulfate through a 30-plate column with full return of reflux for three hours. In the course of this treatment the cyclopentadiene dimerized completely. The catalyzates from different experiments with a given catalyst were united and distilled through a 70-plate column. In all cases this resulted in a head fraction (b.p. up to 41.7°), a piperylene fraction (b.p. 41.7-43.8°), and a residue containing cyclopentadiene dimer and other condensation products. The relative amounts and the properties of the individual fractions are given in Table 2.

Combined head fractions from Experiments No. 1, 5, and 10; 2, 6, and 11; 3, 7, 14, and 25; 4, 8, 20, and 26 were brominated in acetic acid. The products were washed and dehydrated, and unchanged saturated hydrocarbons were then distilled off from a water bath. The bromo compounds were cooled and separated into solid and liquid fractions. The solid bromo compounds were fractionally crystallized from petroleum ether and alcohol, and the liquid bromo compounds were vacuum-distilled. The results obtained are given in Tables 3 and 4.

The properties indicate that pentane and isopentane occurred in the paraffin part, and 1,2,4,5-tetrabromopentane (I) and 1,2,3,4-tetrabromopentane (II) occurred among the solid bromo compounds.

Comparison with the constants in Table 5 indicates that our bromination products are mixtures of dibromopentanes. Hence, in the catalytic transformations of piperylene, the formation of cyclopentadiene is accompanied by the formation of pentanes and pentenes as a result of the redistribution of hydrogen. The effect of the relative proportions of the cis-and trans-forms of piperylene is shown in Table 6. In each of the four experiments we took a fresh portion of catalyst (50 ml) and 40 g of piperylene, in which the relative amounts of the cis-and trans-isomers were varied. The samples of piperylene were obtained by the fractionation of commercial piperylene through a 70-plate column. The experiments were carried out at 600°. The composition of the mixture was determined from its refractive index.

Dependence of the Yield of Cyclopentadiene on Pressure in the Reactions of Piperylene in Contact with $Al_2O_3 + Cr_2O_3$ (1 : 1)

The experiments were carried out at various pressures at a constant space velocity of 0.5 $hour^{-1}$ at 600°. In each experiment we took a fresh portion of catalyst (50 ml) and 80 g of piperylene having n_D^{20} 1.4310. The cyclopentadiene content of the catalyzate was determined, and the catalyzate was then fractionated through a 30-plate column to separate the part boiling up to 44°. The residue was distilled from a Favorsky flask. The results obtained are given in Table 7.

After removal of unsaturated hydrocarbons by treatment with 80% sulfuric acid, the residue from Experiment 8 (b.p. 44-160°) was found to contain benzene, toluene, and o-xylene.

Dependence of the Yield of Cyclopentadiene on the Time of Contact with Platinum-Aluminosilicate Catalyst (6% Pt)

In order to avoid any distortion of results by reduction in activity, before the experiments wer commenced the sequence of oxidation by air and reduction by hydrogen under regeneration conditions was carried out twice. The amount of catalyst was the same (100 ml) in each experiment, and the amount of piperylene (n_D^{20} 1.4330) varied in different experiments from 5 to 60 g. The results of the experiments were used for the calculation of rate constants from Panchenkov's equation for the kinetics of a reaction occurring in a continuous system [10], the particular case taken being that of strong adsorption:

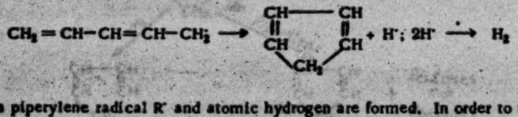
$$k = \frac{nx}{l},$$

in which k is the rate constant, n is the number of moles of piperylene passing into the reaction zone in unit time, x is the degree of conversion, and l is the length of the reaction zone filled with catalyst – in our case 40 cm. The experimental conditions and the values of the constants are given in Table 8. At 600° and space velocities of 0.06 and 0.1 $hour^{-1}$, the amounts of cyclopentadiene formed were 0.00852 and 0.0115 mole, respectively, the degrees of conversion being 0.138 and 0.117 (Fig. 2). The average values of the constants were determined: for 550° K $8.03 \cdot 10^{-5}$ mole/cm, and for 600° K $5.41 \cdot 10^{-4}$ mole/cm. Substitution of these values in the Arrhenius equation yielded a value of 59,105 cal/mole for the activation energy; since the adsorption is strong, the activation energy is true activation energy.

Mechanism of the Formation of Cyclopentadiene

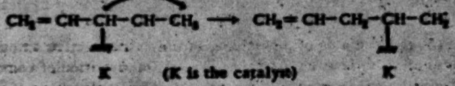
The only reported suggestion regarding the mechanism of the cyclization of piperylene was made quite recently [2]. According to this, the reaction goes in two stages:

$$CH_2{=}CH{-}CH{=}CH{-}CH_3 \longrightarrow CH_2{=}CH{-}CH{=}CH{-}\dot{C}H_2 + H^{\cdot} \qquad (1)$$



(2)

In the first stage a piperylene radical $R^{\cdot}$ and atomic hydrogen are formed. In order to form an idea of the actual mechanism of the reaction it is necessary to take into account the kinetic data concerning the reaction, the presence in the reaction products of pentanes and pentenes and the absence of cyclopentene, the catalytic character of the reaction, the presence in the reaction products (in some experiments) of 1,4-pentadiene, and the occurrence of an upper limit for the yields of cyclopentadiene. On the basis of these data we consider that the reaction goes by a radical mechanism in three stages. In the first stage the piperylene molecule is adsorbed at the 3-4 position on the catalyst surface; as a result a valency is freed at the third carbon atom with formation of a radical, which isomerizes at the β-position, the free valency then passing to the fifth carbon atom:

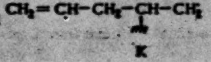

$CH_2{=}CH{-}\underset{K}{CH}{-}CH{-}CH_3 \longrightarrow CH_2{=}CH{-}CH_2{-}\underset{K}{CH}{-}CH_2^{\cdot}$

(K is the catalyst)

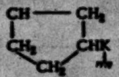
The secondary radical formed may not isomerize, but may be desorbed. This results in cis-trans conversion.

The β-isomerization of radicals has been observed by Voevodsky and Mardaleishvili [11] in a study of deuterium exchange in primary propyl and isobutyl radicals.

The heat of reaction of the first stage of formation and isomerization will be made up of the energy of the rupture of a π-bond (40-45 kcal) and the difference in the energies of bonds formed by hydrogen with a primary and with a secondary carbon atom (about 5 kcal). It will therefore be about 45-50 kcal/mole. On this basis, the activation energy will be 55-60 kcal/mole, which is in close accord with the experimental value (about 60 kcal). The radical

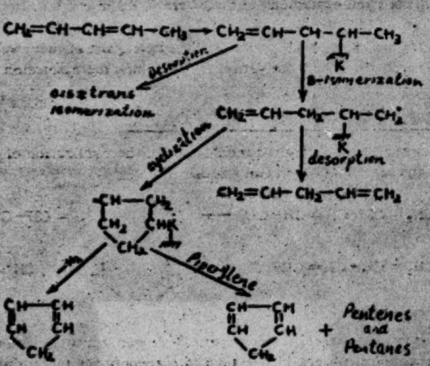

$CH_2{=}CH{-}CH_2{-}\underset{K}{CH}{-}CH_2^{\cdot}$

may be desorbed with formation of 1,4-pentadiene or may undergo intramolecular addition at the double bond with formation of a cyclic radical



(second stage). This stage proceeds with an insignificant activation energy. In the last (third) stage, redistribution of hydrogen between the radical formed in the second stage and piperylene occurs without the consumption of any activation energy; cyclopentadiene, pentenes, and pentanes are then formed. It is probable that to some extent cyclopentadiene is formed directly by dehydrogenation of the radical. The determining stage of the reaction is the first, since it occurs with the highest activation energy. As can be seen from the scheme of formation of the radical and its isomerization at the β-position, this process is analogous to the isomerization of piperylene into 1,4-pentadiene, so that the yield of cyclopentadiene will be determined by the thermodynamic equilibrium piperylene ⇌ 1,4-pentadiene. On the basis of the thermodynamic data of Kilpatrick and coworkers [3] we calculated the 1,4-pentadiene content of such an equilibrium mixture for various temperatures and plotted a curve for the dependence of the 1,4-pentadiene yield on temperature (Fig. 4). On the same diagram we marked the points corresponding to the yields of cyclopentadiene obtained at the same temperatures over various catalysts.

We thus obtain the following scheme for the formation of the transformation products of piperylene:



SUMMARY

1. The effects of various catalysts in the dehydrocyclization of piperylene to cyclopentadiene were investigated.

2. It was shown that the cyclization reaction is catalytic.

3. The activation energy of the process and the rate constants of the reaction at 550° and 600° were determined.

4. It was shown that the yield of cyclopentadiene does not depend on the relative amounts of the cis- and trans-forms present in the original piperylene, but depends on the pressure.

5. A mechanism is proposed for the cyclization reaction of piperylene.

LITERATURE CITED

[1] R. L. Frank, R. D. Emmick, R. I. Johnson, J. Am. Chem. Soc., 69, 2313 (1947).

[2] R. M. Kennedy, S. J. Hetzel, Ind. Eng. Chem., 42, 547 (1950).

[3] I. E. Kilpatrick, C. W. Beckett, E. I. Prosen, M. S. Pitzer, F. D. Rossini, J. Res. Nat. Bur. Stand., 42, No. 3, 225 (1949).

[4] V. V. Korobov and A. V. Frost, Free Energies of Organic Compounds, Mendeleev All-Union Chem. Soc. Press, Moscow, 1950.

[5] Yu. F. Rachinsky and M. Z. Zalmanovich, Collection of Papers on General Chemistry, Vol. 1, Acad. Sci. USSR Press, Moscow, 1953, p. 415.

[6] B. N. Afanasyev, Factory Labs., 14, 1492 (1948).

[7] V. I. Pasevich-Kolyada and M. A. Prilezhaev, J. Gen. Chem., 21, 517 (1951) (T. p. 571)*.

[8] R. Ya. Levina and E. A. Viktorova, J. Gen. Chem., 20, 677 (1950) (T. p. 713)*.

[9] L. S. Dedusenko, Trans. Azerbaidzhan Affil. Inst. Acad. Sci. USSR, No. 3, 87 (1940).

[10] G. M. Panchenkov, J. Phys. Chem., 22, 209 (1948).

[11] N. N. Semenov, Some Problems in Chemical Kinetics and Reactivity, Acad. Sci. USSR Press, Moscow, 1954, pp. 71-72.

Received December 1, 1954

M. V. Lomonosov State University,
Moscow

---

* T. p. = C. B. Translation pagination.

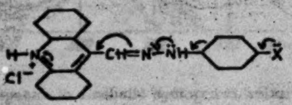
ABSORPTION SPECTRA AND MOLECULAR STRUCTURE

COMMUNICATION 4. EFFECT OF THE CHARACTER OF THE SUBSTITUENT ON COLOR IN DERIVATIVES OF 9-ACRIDINECARBOXALDEHYDE PHENYLHYDRAZONE HYDROCHLORIDE

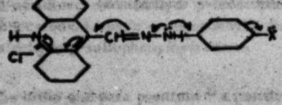
A. A. Kharkharov

Generalization of the widely known theoretical concepts and experimental data that have appeared in the literature on the relationship between color and structure in organic compounds enables us to conclude that the color of organic compounds depends primarily on the presence of electron-donating and electron-accepting centers in the molecule and on the number of interacting π-electrons (in particular, on the length of the conjugated chain). This conclusion is in close accord with the experimental data presented in this paper on the effect of the character of the substituent on color in para-substituted derivatives of 9-acridinecarboxaldehyde phenylhydrazone hydrochloride.

As the length of the conjugated chain is almost constant in most of these compounds, the displacement in the principal absorption maximum should vary regularly with change in the electron-donating or electron-accepting properties of the substituent. Hence, the greater the tendency of the substituent to repel electrons:



the greater (other things being equal) should be its bathochromic effect and, on the other hand, the greater the tendency of the substituent to attract electrons:



the greater should be its hypsochromic effect. As is well known [1-6, 9], increase in the length of the conjugated chain is always accompanied by a displacement of the principal absorption maximum toward the longer waves, as will be shown below.

From the data in the table and in Fig. 1 on the absorption spectra of derivatives of 9-acridinecarboxaldehyde phenylhydrazone hydrochloride it will be seen that the nitro group ($\Delta \lambda = -40$ mμ) is the most powerful hypsochromic substituent. The reason for this lies in the fact that nitrogen, and particularly oxygen, attracts electrons more strongly than carbon does. The inductive displacement of electrons, therefore, will be directed from the benzene nucleus to nitrogen and oxygen, which will result in a reduction in the electron density of the carbon atoms of the benzene ring. The displacement of electrons in this direction is facilitated also by the presence of a coordinate link in the nitro group with positive charge on the nitrogen.

Finally, the oxygen of the nitro group is bound to nitrogen by a double bond. The π-electrons of this double bond interact with those of the benzene ring, and through them with the free pair of electrons on the hydrazone NH group, with formation of a unified electron cloud. As a result of a combination of all these effects, on all of

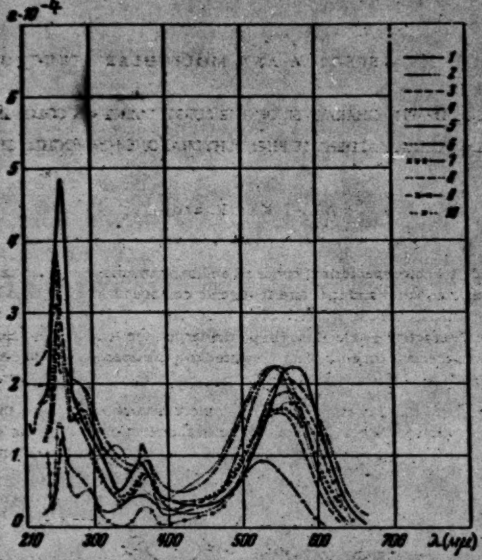


Fig. 1. Absorption spectra in alcoholic hydrogen chloride: 1) 9-acridinecarboxaldehyde phenylhydrazone; 2) 9-acridinecarboxaldehyde p-sulfamoylphenylhydrazone; 3) 9-acridinecarboxaldehyde p-acetylphenylhydrazone; 4) 9-acridinecarboxaldehyde p-formylphenylhydrazone; 5) 9-acridinecarboxaldehyde p-carboxphenylhydrazone; 6) 9-acridinecarboxaldehyde p-iodophenylhydrazone; 7) 9-acridinecarboxaldehyde p-chlorophenylhydrazone; 8) 9-acridinecarboxaldehyde p-bromophenylhydrazone; 9) 9-acridinecarboxaldehyde p-nitrophenylhydrazone; 10) 9-acridinecarboxaldehyde p-sulfophenylhydrazone.

the carbon atoms — particularly those in the ortho and para positions — a positive charge will appear, which, in its turn, will attract electrons from the NH group, i.e. will oppose the displacement of electrons in the direction from benzene nucleus to the acridine nitrogen [6].

The second among the substituents studied with respect to hypsochromic effect is the aldehyde group ($\Delta\lambda = -23$ mμ; see table and Fig. 1); its powerful electron-accepting properties are associated with the presence of an oxygen atom attached to carbon by a double bond. The oxygen strongly attracts electrons both by the induction mechanism (according to its position in the Mendeleev system), and also by the conjugation mechanism. The hydrogen of the aldehyde group, unlike the methyl of the acetyl group ($\Delta\lambda = -22$ mμ; see table and Fig. 1), does not lower the positive charge on the carbon atom appreciably. Replacement of the aldehyde group by hydroxyl, i.e. when we pass to carboxyl ($\Delta\lambda = 16$ mμ; see table and Fig. 1), leads to quite an appreciable neutralization of the charge on the carbon and to a weakening of the electron-accepting properties of the group.

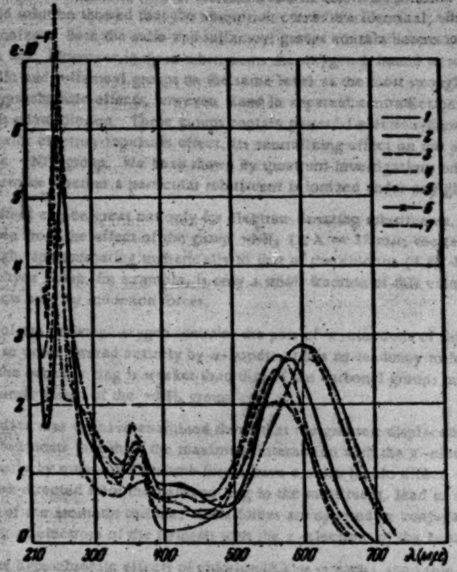
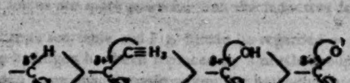


Fig. 2. Absorption spectra in alcoholic hydrogen chloride: 1) 9-acridinecarboxaldehyde p-methoxyphenylhydrazone; 2) 9-acridinecarboxaldehyde p-tolylhydrazone; 3) 9-acridinecarboxaldehyde phenylhydrazone; 4) 9-acridinecarboxaldehyde p-iodophenylhydrazone; 5) 9-acridinecarboxaldehyde p-thiocyanatophenylhydrazone; 6) 9-acridinecarboxaldehyde p-acetamidophenylhydrazone; 7) 9-acridinecarboxaldehyde p-ethoxyphenylhydrazone.

In the ionized state, the carboxyl group has a more feeble electron-accepting effect than it has in the nonionized state. The electron-accepting properties of carbonyl compounds fall in the sequence:



The electron-accepting power of a carbonyl-containing substituent is determined by the value of the positive charge (δ+) on the carbon of the carbonyl group. The value of this charge depends on the properties of the radicals attached to the carbonyl group. The more powerful the electron-donating effects of these radicals, the smaller the positive charge (δ+) remaining on the carbon of the carbonyl group and the weaker the electron-accepting properties of the substituent containing the carbonyl group.

Comparison between the hypsochromic effects of the sulfamoyl and sulfo groups (Δ λ = −22 and −5 mμ, respectively; see table and Fig. 1) shows that the first of these has the stronger electron-accepting effect:

Comparison of the colors of internal salts of sulfonic acids in alcoholic solution with those of the sulfonic acids in hydrochloric acid solution showed that the absorption curves are identical, which indicates that in both cases the sulfo group is ionized. Both the sulfo and sulfamoyl groups contain hetero atoms having higher affinity for electrons than carbon has. Moreover, in these substituents the oxygen is bound to sulfur by a coordinate link. This should place the sulfo and sulfamoyl groups on the same level as the most strongly electron-attracting substituents. Their lower hypsochromic effects, however, stand in apparent contradiction to this conclusion. Closer examination removes this contradiction. These groups contain powerful electron-donating substituents: $-NH_2$ and $-O^-$. As $-O^-$ has the greater electron-repulsion effect, its neutralizing effect on the positive charge on the sulfur is greater than that of the $-NH_2$ group. We have shown by spectrum investigations on the sulfo and other groups that it is possible to determine whether a particular substituent is ionized under any given conditions.

The conjugation effect can be great not only for electron-donating substituents, but also for electron-accepting substituents, as can be seen from the effect of the group $-\overset{+}{N}H_3$ ($\Delta\lambda = 12$ mμ, see table). The positive charge of this substituent is very high, approximating numerically to that of the electron ($4.80 \cdot 10^{-10}$ esu), whereas the charge on the carbon of the aldehyde group, for example, is only a small fraction of this value. Also, unlike the aldehyde group, the $-\overset{+}{N}H_3$ group acts only by induction forces.

Whereas the octet of the carbonyl oxygen includes the pair of π-electrons of the carbon-oxygen bond, the ammonium nitrogen has an octet formed entirely by σ-bonds; it has no tendency to form a ten-electron shell, so that its interaction with the benzene ring is weaker than that of the carbonyl group; in this lies the source of the relatively weak hypsochromic effect of the $-\overset{+}{N}H_3$ group.

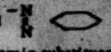
The experimental data that we have examined shows that the greatest displacement of the principal absorption maximum is found for substituents that show the maximum interaction with the π-electrons of the conjugated system. The groups that interact only by means of Coulomb forces have a more feeble effect. In halogen derivatives, the induction forces, which are directed from the benzene ring to the substituent, lead to a reduction in the electron densities of the carbon atoms of the aromatic residue; these forces are opposed by conjugation forces arising from the interaction of the free pair of electrons of the halogen with the π-electrons of the benzene ring.

The examples of the hypsochromic effects of chlorine ($\Delta\lambda = -8$ mμ; see table and Fig. 1) and bromine $\Delta\lambda = -2$ mμ; see table and Fig. 1) show particularly clearly that the electron displacement occurs in the direction of the element belonging to the higher group of the periodic system and that within a given group of the periodic system the atom having the lower volume has the more pronounced electron-donating character.

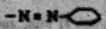
As a result of the great difference in charge between carbon and chlorine, the inductive hypsochromic effect of chlorine predominates over its conjugative bathochromic effect. However, for iodine substituted in the para postion ($\Delta\lambda = +2$ mμ; see table and Fig. 2), the reverse effect is observed. Here the conjugative bathochromic effect suppresses the inductive hypsochromic effect. An accumulation of quantitavtive changes results in a qualitative change. As a rule, substituents having a free pair of electrons on the atom that is directly attached to the aromatic nucleus have bathochromic effects. Some substituents of this sort (amino and hydroxy groups, and their derivatives), as already noted above, have been called auxochromes. The example of the halogens shows that this situation is maintained only when the conjugative forces are more powerful than the inductive forces.

The group $-\overset{\curvearrowleft\curvearrowright}{S}-C\equiv N$ ($\Delta\lambda = -3$ mμ; see table and Fig. 2) can be regarded as a combination of two substituents: as a thiol group in which the hydrogen has been replaced by a nitrile group. The thiol group has an unshared electron pair and is to be regarded as an auxochromic group: its bathochromic effect is not less than that of the hydroxy group. On the contrary, the nitrile group is one of the most powerful electron-accepting substituents. For example, the dipole moment of the nitrile group is between those of the nitro and aldehyde groups. The behavior of the $-S-C\equiv N$-group is very reminiscent of that of the halogens. The nitrile group neutralizes the electron-donating character of the sulfur almost completely, so that the $-S-C\equiv N$-group is found to have only a very weak bathochromic effect.

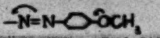
The examples that we have analyzed show that a molecule taken as a whole, and also an individual substituent, should be regarded as a dialectical unity of opposites, as a unity of attractive and repulsive forces.

In the groups $-CH=N-NH-$ ($\Delta\lambda = +8$ mμ, see table) and  $-N=N-$ ($\Delta\lambda = +17$ mμ, see table) – like the $-S-CN$ group and iodine atom, and most of the other bathochromic substituents – conjugation forces predominate over induction forces. In this case we have a substituent containing a double bond, which acts bathochromically by lengthening the conjugated chain [2]. This bathochromic effect readily hides any hypsochromic effect associated with a displacement of electrons from the benzene nucleus to the nitrogen atoms of the azo group (on account of the position of nitrogen in the periodic system).

The further deepening of color from phenylazo (Δ λ = + 17 mμ, see table) [6]:

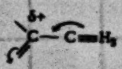


to p-methoxyphenylazo (Δλ = + 28 mμ, see table)



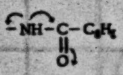
is to be associated with the inclusion of the OCH$_3$ group in the conjugated chain.

The methyl group (Δλ = + 18 mμ, see Fig. 2 and table)

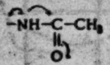


has a bathochromic effect as a result of the marked conjugation of σ, π -electrons [7, 8]. It is an electron-donating substituent and assists the acridinium nitrogen to change the electron densities of all the atoms of the system, with the participation of the free electron pair of the — NH — group.

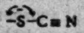
The benzamido group (Δλ = 34 mμ):



and the acetamido group (Δ λ = 36 mμ; see Fig. 2 and table):

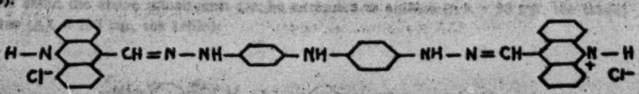


like the thiocyanato group:



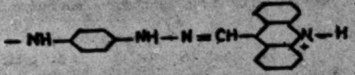
are combinations of pairs of substituents: the amino group and the benzoyl or acetyl group. The amino group contains an unshared pair of electrons and is one of the most powerful electron-donating groups; more powerful, in fact, than the thiol group. On the other hand, benzoyl and acetyl have marked electron-accepting properties. They are however weaker in this respect than the nitrile group, so that the electron-donating properties of the benzamido and acetamido groups are considerably more marked than those of the thiocyanato group. Correspondingly, there is a much greater displacement of the absorption maximum (Δλ) for 9-acridinecarboxaldehyde p-benzamido- and p-acetamido-phenylhydrazones (as hydrochlorides) than for the corresponding p-thiocyanatophenylhydrazone.

Nevertheless, the acid residues reduce the electron-donating effect of the amino group to such an extent that its bathochromic effect becomes less than that of the hydroxyl group (Δ λ = 48 mμ). We meet a similar phenomenon in the case of bis (9-acridinecarboxaldehyde) (iminodi -p-phenylene) dihydrazone dihydrochloride (Δ λ = − 2 mμ; see table and Fig. 3):



This compound can be regarded as the salt of the cation of 9-acridinecarboxaldehyde phenylhydrazone containing an amino substituent the hydrogen of which is replaced by a residue of a 9-acridinecarboxaldehyde phenylhydrazone cation.

The substituent:



has powerful electron-accepting properties, and it attracts the free electron pair so strongly that the substituted amino group must be regarded, like chlorine, as an electron-accepting substituent, in spite of its free electron pair.

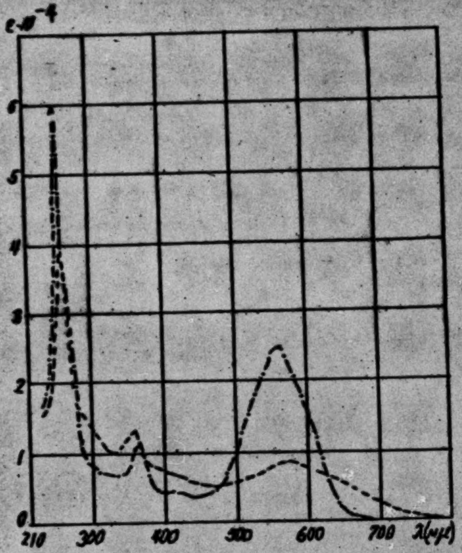
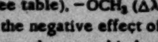


Fig. 3. Absorption spectra in alcoholic hydrogen chloride: — · — · bis (9-acridinecarboxaldehyde) (iminodi-p-phenylene) dihydrazone; — — — 9-acridinecarboxaldehyde phenylhydrazone

In groups $-OH$ ($\Delta\lambda = +48$ mμ; see table), $-OCH_3$ ($\Delta\lambda = +48$ mμ; see Fig. 2 and table), and $-OC_2H_5$ ($\Delta\lambda = +48$ mμ; see Fig. 2 and table), the negative effect of the induction forces is more than overcome by conjugation forces, and it is the relation between these two kinds of forces that determines the positions of these groups among bathochromic substituents.

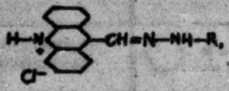
The identity in the values of the displacement of the principal absorption maximum of 9-acridinecarboxaldehyde phenylhydrazone hydrochloride due to the introduction of a hydroxyl, a methoxyl, and an ethoxyl group indicates that under the conditions of measurement the hydroxyl group is in the unionized state. The difference in the effects of hydrogen and alkyl is so slight that we were unable to detect it.

All that we have said about the above substituents can be extended to anilino ($\Delta\lambda = 93$ mμ, see table) $-NHC_6H_5$ and to p-anisidino ($\Delta\lambda = 153$ mμ, see table):



TABLE

Displacement of the Principal Absorption Maximum in Derivatives of 9-Acridinecarboxaldehyde Phenylhydrazone Hydrochloride



containing a Substituent in the para-Position to the NH Group

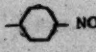
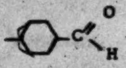
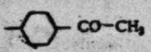
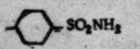
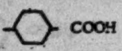
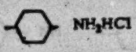
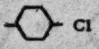
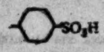
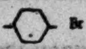
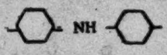
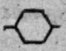
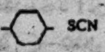
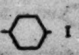
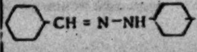
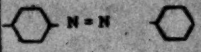
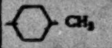
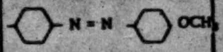
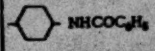
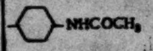
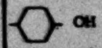
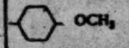
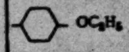
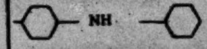
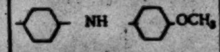
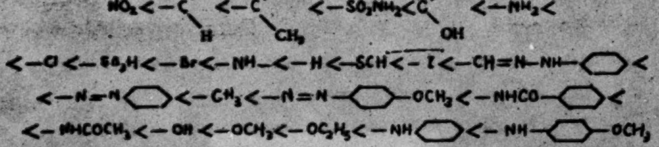
Number	Name of substance	R	Long-wave absorption maximum (mμ)	Displacement of absorption maximum Δλ (mμ)
1	9-Acridinecarboxaldehyde p-nitrophenylhydrazone hydrochloride		522	−40
2	9-Acridinecarboxaldehyde p-formylphenylhydrazone hydrochloride		539	−23
3	9-Acridinecarboxaldehyde p-acetylphenylhydrazone hydrochloride		540	−22
4	9-Acridinecarboxaldehyde p-sulfamoylphenylhydrazone hydrochloride		540	−22
5	9-Acridinecarboxaldehyde p-carboxyphenylhydrazone inner salt		546	−12
6	9-Acridinecarboxaldehyde p-aminophenylhydrazone dihydrochloride		550	−12
7	9-Acridinecarboxaldehyde p-chlorophenylhydrazone hydrochloride		554	− 8
8	9-Acridinecarboxaldehyde p-sulfophenylhydrazone inner salt		557	− 5
9	9-Acridinecarboxaldehyde p-bromophenylhydrazone hydrochloride		560	− 2
10	Bis(9-Acridinecarboxaldehyde)(iminodi-p-phenylene)dihydrazone dihydrochloride		560	− 2
11	9-Acridinecarboxaldehyde phenylhydrazone hydrochloride		562	0
12	9-Acridinecarboxaldehyde p-thiocyanatophenylhydrazone hydrochloride		565	3
13	9-Acridinecarboxaldehyde p-iodophenylhydrazone hydrochloride		566	4
14	9-Acridinecarboxaldehyde α-(phenylhydrazono)-p-tolylhydrazone hydrochloride		570	8

TABLE (continued)

Number	Name of substance	R	Long-wave absorption maximum (mμ)	Displacement of absorption maximum Δλ (mμ)
15	9-Acridinecarboxaldehyde p-phenylazophenylhydrazone hydrochloride		579	17
16	9-Acridinecarboxaldehyde p-tolylhydrazone hydrochloride		580	18
17	9-Acridinecarboxaldehyde p-(p-methoxyphenylazo)phenylhydrazone hydrochloride		590	28
18	9-Acridinecarboxaldehyde p-benzamidophenylhydrazone hydrochloride		596	34
19	9-Acridinecarboxaldehyde p-acetamidophenylhydrazone hydrochloride		598	36
20	9-Acridinecarboxaldehyde p-hydroxyphenylhydrazone hydrochloride		610	48
21	9-Acridinecarboxaldehyde p-methoxyphenylhydrazone hydrochloride		610	48
22	9-Acridinecarboxaldehyde p-ethoxyphenylhydrazone hydrochloride		610	48
23	9-Acridinecarboxaldehyde p-anilinophenylhydrazone hydrochloride		655	93
24	9-Acridinecarboxaldehyde p-(p-anisidino)phenylhydrazone hydrochloride		715	153

The exceptionally high bathochromic effects of these substituents are associated with the fact that their entry into the dye molecule is accompanied by considerable lengthening of the conjugated chain and by marked electron-donating properties.

Thus, the effects of all of the substituents that we have investigated can be arranged in the following sequence (see table):



NO2 < —C(=O)H < —C(=O)CH3 < —SO2NH2 < C(=O)OH < —NH2 <
< —Cl < —SO3H < —Br < —NH— < —H < —SCH < —I < —CH=N—NH— <
< —N=N < —CH3 < —N=N— —OCH3 < —NHCO— <
< —NHCOCH3 < —OH < —OCH3 < —OC2H5 < —NH < —NH— —OCH3

This sequence, which is derived from experimental results, is in accord with the concepts regarding the structures and properties of organic molecules that have been developed by Soviet chemists.

EXPERIMENTAL

The spectrum investigations were carried out with an SF-1 photoelectric spectrophotometer over the range 210-800 mμ. The solvent used was 0.2 N alcoholic hydrogen chloride. Effects due to solvent were excluded. In the spectrum measurements, all of the dyes were used at the same concentration. All of the substances were prepared under the conditions used previously for the preparation of 9-acridinecarboxaldehyde phenylhydrazone; their purities were checked by their nitrogen contents, determined by combustion. The results of the spectrum investigations are given in Figures 1, 2, and 3 and in the table. More detailed information about the compounds discussed in this paper will be given in a future communication.

SUMMARY

1. It is shown that the presence of a substituent in the phenyl nucleus of 9-acridinecarboxaldehyde phenylhydrazone hydrochloride has a very great influence on its color.

2. A study of the absorption spectra of these compounds provides convincing evidence that the color of organic substances depends essentially on the presence of electron-donating and electron-accepting centers and on the number of interacting π-electrons (in particular, on the length of the conjugated chain). The more marked the opposing characters of the groups or atoms linked through the conjugated chain, the more powerful their bathochromic effect. On the other hand, the greater the electron-accepting power of the substituent in the phenyl group of 9-acridinecarboxaldehyde phenylhydrazone hydrochloride, the greater its hypsochromic effect. Increase in the length of the conjugated chain always acts bathochromically.

3. The absorption spectra of para-substituted phenylhydrazones of 9-acridinecarboxaldehyde hydrochloride were determined in the wavelength range 210-800 mμ, and the batho- or hypso-chromic effects of 22 substituents were determined

LITERATURE CITED

[1] A. N. Terenin, V. N. Kondratyev, I. L. Knunyants, M. I. Kabachnik, N. D. Soklov, and O. A. Reutov, State of the Theory of Chemical Structure in Organic Chemistry, Acad. Sci. USSR Press, 1954, p. 32.

[2] A. E. Porai-Koshits, Selected Works, Acad. Sci. USSR Press, 1949.

[3] V. A. Izmailsky, Trans. Fourth Conference Aniline Dye Chem. and Tech., Acad. Sci. USSR Press, 1940, p. 41.

[4] V. A. Ismailsky, Trans. Eighth Conference Aniline Dye Chem. and Tech., Acad. Sci. USSR Press, 1950, p. 88.

[5] A. N. Terenin, Photochemistry of Dyes, Acad. Sci. USSR Press, 1947.

[6] A. A. Kharkharov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 1 117. (T.p. 95).*

[7] A. N. Nesmeyanov, Sci. Mem. Moscow State Univ.,132, 5, 1950.

[8] A. A. Kharkharov, J. Gen. Chem., 23, 1175 (1953). (T.p. 1235).*

[9] A. I. Kiprianov, Ukrainian Chem. J., 4, 340, (1952).

Received November 30, 1954

S. M, Kirov Textile Institute
Leningrad

---

* T.p. = C. B. Translation pagination

BLANK
PAGE

IDENTIFICATION OF HYDROCARBONS WITH THE AID OF DISPERSION CURVES

I. V. Obreimov and T. N. Shkurina

Dispersion curves determined over a wide range of wavelengths can be used as criteria in the identification of organic substances. There have been only a few investigations on the determination of dispersion curves in the ultra-violet region of the spectrum. Systematic measurements over a wide range of wavelengths were first made by Anri [1] and Voellmy [2], who used the compensating prism method. These authors, unfortunately, do not give their primary data. Individual organic substances have been investigated by Allsopp [3] and by Lowry and Allsopp [4] by the interferometric method. The work of Friberg [5] is also of interest: he made dispersion measurements with the interferometer on the gaseous hydrocarbons methane, ethane, propane, butane, and ethylene.

EXPERIMENTAL

The refractive indices of the hydrocarbons investigated were determined over a wide range of wavelengths (6500-2500 A) by the Fresnel diffraction method [6, 7]. A parallel beam of white light was passed through a plate having plane parallel sides and immersed in the liquid. A part of the beam passed through the plate, and part through the liquid. Along the edge of the geometric shadow from the plate, the interference of the two beams was to be observed. The shadow of the edge of the plate fell on the slit of a spectrograph, and in the focal plane of the spectrograph the picture shown in Fig. 1 was to be observed.

The center of each dark spot corresponds to a wavelength for which $\underline{N}$ is equal to an odd number of half-waves, and the bright interval between spots corresponds to a wavelength for which N is a whole number. Integral values of $\underline{N}$ from $\underline{N}$ – 117 to $\underline{N}$ – 120 are indicated by dots. The refractive index $\underline{n}$ of 1,5-hexadiene increases more slowly than that of quartz. With further increase in frequency, the refractive index of 1,5-hexadiene increases more rapidly than that of quarts, and the numbers begin to decrease. There is a corresponding change in the slope of the diffraction spots.

By measuring the number of diffraction spots we can estimate the variation in the refractive indices of liquids. The refractive index was calculated according to the formula:

$$n_1 = n_q + \frac{N\lambda}{d}, \tag{1}$$

in which n_1 is the refractive index of the liquid, n_q is the refractive index of the quartz, $\underline{N}$ is the number of the diffraction spot, λ is the wavelength, and $\underline{d}$ is the thickness of the standard quartz plate.

An ISP-22 spectrograph was used in the investigation. The source of ultraviolet radiation was provided by a super-high pressure krypton lamp. A diagram of the experimental arrangement is given in Fig. 2. The design of the cell is shown in Fig. 3. The standard quartz plate was fixed by means of a trace of fish glue to the inner surface of the quartz window of the cell. The thickness $\underline{d}$ of the plate was 1.0635 mm•.

The thickness of the layer of liquid between the windows of the cell was about 9 mm. The cell was fixed in front of the slit of the spectrograph on a special holder. This cell holder was pivoted, so that the plate could be placed strictly perpendicular to the beam from the collimator. Adjustment for perpendicularity was carried out by the autocollimation method.

If the diffracting edge of the block is parallel to the horizontal slit illuminated by the light source and perpendicular to the vertical slit of the spectrograph, then the diffraction picture (as shown in Fig. 1) will take the form

---

• The dispersion curve for the standard plate was determined jointly by the Kiev Institute of Physics of the Academy of Sciences of the Ukrainian SSR and the Institute of Organic Chemstry of the Academy of Sciences of the USSR; it will be published in the near future.

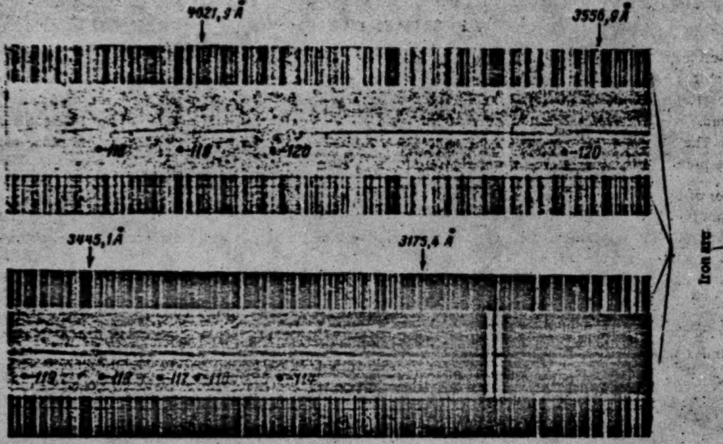

4021,9 Å
3556,9 Å
110
118
120
120
3445,1 Å
3175,4 Å
119
118
117
116
114
Iron arc

Fig. 1. Diffraction picture of 1,5-hexadiene-quartz.

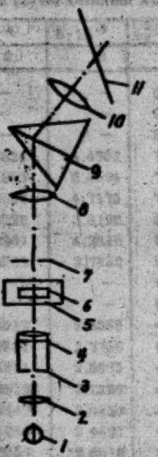


Fig. 2. Diagram of experimental arrangement: 1) light source; 2) quartz condenser; 3) collimator having an archromatic quartz-fluorite objective; 4) objective; 5) cell with plane windows for liquid under investigation; 6) quartz-glass plate having parallel plane sides; 7) slit of the ISP-22 spectrograph; 8 and 10) objectives; 9) prism; 11) photographic plate.

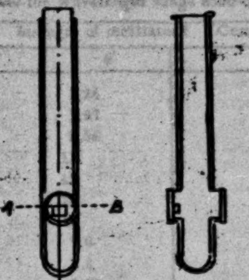


Fig. 3. Refractometric cell. The face AB of the standard plate is ground and polished in a plane strictly perpendicular to the parallel sides, and there are no bevels on the edges.

of drawn-out oval spots. Above and below in Fig. 1 the spectrum of the iron arc is shown. In the center will be seen the diffraction picture – drawn out into a spectrum – due to the side phase of the quartz block, which is here immersed in 1,5-hexadiene.

The number of the diffraction spot corresponding to λ = 5893 A was determined by direct calculation from the value of the refractive index obtained on an Abbe refractometer; n is then obtained accurate within $1 \cdot 10^{-4}$, and the whole dispersion curve will be accurate within not less than $1\text{-}2 \cdot 10^{-4}$.

Substances Investigated

The substances selected for investigation were saturated hydrocarbons having straight and branched chains, unsaturated hydrocarbons including compounds having conjugated double bonds, and cyclolkanes: 1) hexane, b.p. 68.7-68.8° (760 mm); d_4^{20} 0.6594; n_D^{20} 1.3751; 2) heptane, b.p. 98.3-98.4° (760 mm); d_4^{20} 0.6834; n_D^{20} 1.3878; 3) octane, b.p. d_4^{20} 0.7026; n_D^{20} 1.3974; 4) 2,2,4-trimethylpentane, b.p. 99.6-99.7° (760 mm); d_4^{20} 0.6908; n_D^{20} 1.3925; 5) 1-hexene, d_4^{20} 0.6734; n_D^{20} 1.3925; 6) 1-heptene, b.p. 92.8-92.9° (745 mm); d_4^{20} 0.6971; n_D^{20} 1.4001; 7) 1-octene, d_4^{20} 0.7160; n_D^{20} 1.4130; 8) 2,2,4-trimethylpentene (mixture 1- and 2-pentene derivatives), b.p. 102.4-102.8° (752 cm); n_D^{20} 1.4130; 9) cyclopentane, b.p. 49.5-49.8° (755.7 mm); d_4^{20} 7556; n_D^{20} 1.4063; 10) methylcyclopentane, b.p. 71.0° (737.8 mm); d_4^{20} 0.7485; n_D^{20} 1.4110; 11) 1,5-hexadiene, b.p. 59-60°; d_4^{20} 0.6945; n_D^{20} 1.4040; 12) isoprene, d_4^{20} 0.6806; n_D^{20} 1.4202; 13) mixture of dipentene and diprene, b.p. 173.8-174.8°; d_4^{20} 0,8436; n_D^{20} 1.4735; 14) alloocimene, b.p. 79° (11 mm); n_D^{15} 1,5450, [illegible]

Hexane, heptane, octane, 2,2,4-trimethylpentane, 1-hexene, 1-heptene, and 1,5-hexadiene were obtained from the Catalytic-Synthesis Laboratory of the Zelinsky Institute of Organic Chemistry of the USSR Academy of Sciences, 2,2,4-trimethylpentene from the Pyrogenic-Processes Laboratory of the same institute, isoprene and the mixture of dipentene and diprene from the Unsaturated-Compounds Laboratory of the same institute, 1-octene, 2,2,4-trimethylpentene, cyclopentane, and methylcyclopentane from the Organic-Catalysis Laboratory of the same institute, and alloocimene from B. A. Arbuzov. To all those who provided these compounds we wish to express our warmest thanks.

Experimental Results

1. Temperature. The refractive indices of liquids are greatly dependent on temperature; for a change of temperature of about 1°, the refractive index of an organic liquid may be reduced by about $5 \cdot 10^{-4}$. For some liquids we measured the dispersion curve at two temperatures differing by 2-3°. It was found that dispersion curves for different temperatures can be brought into coincidence by the addition of a quantity that is the same for all

TABLE 1

Constants of the Dispersion Formula (2) for Different Aliphatic Hydrocarbons over the Wavelength Range 6500-2500 A

Substance	A	$B\cdot10^{-9}$	$\nu_0^2\cdot10^{-9}$	γ_0 cm · 10^3	Strength of oscillator f	Corrections
1	2	3	4	5	6	7
Methane *	–	–	9.638	1.04	1.24	–
Ethane *	–	–	9.355	1.07	1.97	–
Propane *	–	–	8.382	1.10	2.56	–
Hexane	1.2526	4.4702	7.2904	1.17	11	0
Heptane	1.1953	5.4594	7.7673	1.14	15	0
Octane	1.2683	4.7170	7.1614	1.18	13	0
2,2,4-Trimethylpentane	1.3228	3.8192	6.5211	1.24	12	0
Cyclopentane	1.2901	4.3816	6.6782	1.22	7.6	0
Methylcyclopentane	1.3281	3.7382	5.9407	1.30	7.8	0
Ethylene*	–	–	6.906	1.45	0.74	–
Propene*	–	–	6.716	1.49	0.90	–
1-Hexene	1.4019	2.3555	4.7815	1.45	5.5	0
1-Heptene	1.3831	2.7756	5.1135	1.40	7.3	0
1-Octene	1.4211	2.6875	4.9732	1.42	7.9	0
2,2,4-Trimethylpentene	1.4613	2.2327	4.5072	1.49	6.8	0
1,5-Hexadiene	1.4147	2.0810	4.0429	1.57	4.7	0
Dipentene-diprene mixture	1.5250	2.4491	4.0844	1.57	6.5	0
Isoprene	1.6057	2.8019	2.2406	2.11	1.5	C
Alloocimene	1.8650	0.5599	1.3813	2.67	1.8	C

---

*The data for the gaseous hydrocarbons - methane, ethane, propane, ethylene, and propene - are taken from Friberg's paper [5].

wavelengths, i.e. the two dispersion curves can be brought into coincidence by a parallel displacement. In other words, dn/dt is independent of λ (over the range 6500-2500 A). This result is confirmed by available data on the dependence of refractive indices of quartz glass on temperature [8]. In our further considerations all values of n will be reduced to 20°.

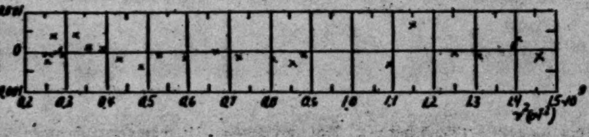


Fig. 4. Correction curve for 1-octene

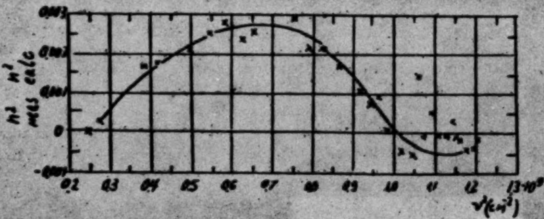


Fig 5. Correction curve for isoprene

2. Interpolation of Values of Refractive Index. Through all experimental values of n, interpolation curves based on a formula of the Sellmeier type were drawn; the formula has three constants:

$$n^2 = A + \frac{B}{\nu_0^2 - \nu^2} \qquad (2)$$

ν being the wave number, and A, B, and ν_0 constants. Data for the dispersions of the liquids studied are given in Table 1*.

3. Determination of Intermediate Values of n with the aid of Formula (2). As a result of measurements of n we obtain an enormous number of experimental points, and the recording of these would occupy a very large space. As there are no generally recognized rules for the recording of the results of dispersion measurements, we propose to use two methods. The first of these is to give a formula of type (2) together with correction curves. Figures 4, 5, and 6 give the correction curves for 1-octene, isoprene, and alloocimene. As will be seen from Fig. 4, formula (2) gives a close rendering of the course of the dispersion curve for 1-octene over the wavelength range 6500-2500 A, and it can be used directly for the calculation of values of n at intermediate wavelengths. Substances for which formula (2) can be used directly for determining intermediate values of n are indicated in the seventh column of Table 1 by the symbol 0.

TABLE 2

Refractive Indices of Hexane at 20°

λ (A)	$\nu = 1/\lambda^2$	n^2	n
6500	2.3669	1.8863	1.3734
6400	2.4414	1.8870	1.3737
6300	2.5195	1.8877	1.3739
6200	2.6015	1.8885	1.3742
6100	2.6874	1.8892	1.3745
6000	2.7778	1.8900	1.3748
5900	2.873	1.8909	1.3751
5800	2.973	1.8918	1.3754
5700	3.078	1.8928	1.3758
5600	3.189	1.8938	1.3761_5
5500	3.306	1.8949	1.3765_5
5400	3.429	1.8960	1.3769_5
5300	3.560	1.8972	1.3774
5200	3.698	1.8985	1.3778
5100	3.845	1.8999	1.3784
5000	4.000	1.9014	1.3789_5

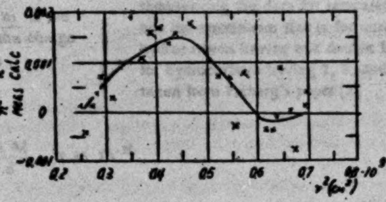


Fig. 6. Correction curve for alloocimene

Table 2 gives values of the refractive index of hexane calculated from formula (2) and the data in Table 1.

In order to obtain intermediate values of n for isoprene and alloocimene, it is necessary to use formula (2) with the addition of a correction taken from the curves of Figure 5 and 6. Substances for which a correction curve must be used in calculating n by formula (2) are indicated in Table 1 by the letter C. Hence, by the aid of Table 1 and the correction curves, the reader can compile a table of refractive indices for the wavelength range in which he is interested.

It will be seen from Figures 4, 5, and 6 that n^2 calculated from formula (2) and corrected as necessary, is obtained accurate within $\pm 5 \cdot 10^{-4}$. The second method is to give values of the refractive index for standard wavelengths. In the visible region of the spectrum we have the Fraunhofer lines C, D, F, and G', which are generally accepted as standards, and to these we propose to add the mercury wavelengths 4046.56, 3650.15, 3478.10, 3131.83, 2967.27, 2536.519, and 2482.8 A, which are often present in the light source. Table 3 shows this method of recording the dispersion curve.

4. Extrapolation of the Results. The interpolation formula (2) is Sellmeier's dispersion formula, which was deduced on the assumption that the dispersing medium is a gas having a single absorption band of frequency ν_0 and

---

* In a previous paper [7] we interpolated the value of the molecular refraction MR with the aid of Sellmeier's formula in order to enable us to collate our measurements with those of Voellmy. The values of f given there cannot, of course, be similar to those calculated in the present investigation; the calculations were done only in order to demonstrate that the values were high.

TABLE 3

Refractive Indices of Hexane Calculated for Standard Wavelengths from the Data of Table 1

Spectrum line	n	Spectrum line	n
C	1.3733_5	3650.15 A	1.3914_5
D	1.3751_5	3131.83 A	1.4019_5
F	1.3797	2967.28 A	1.4254_5
G'	1.3834_5	2536.52 A	1.4254_5
4046.56 A	1.3863_6	2482.82 A	1.4297

the dispersion is measured in a region of the spectrum appreciably removed from ν_0, i.e. at a point at which absorption is low. The term A is associated with the effect of all the other absorption bands, which are considered to be even more far-removed than the band ν_0. The coefficient B in Sellmeier's formula is related to the effective strength of the oscillator of the ν_0 band by the formula:

$$B = f\,\frac{Ne^2}{\pi m c^2}, \tag{3}$$

in which f is the effective strength of the oscillator, m is the mass of the electron, c is the velocity of light, e is the charge on the electron, and N is the number of molecules in 1 c.c $= \frac{6.02 \cdot 10^{23}}{M}$ d (M is the molecular weight)

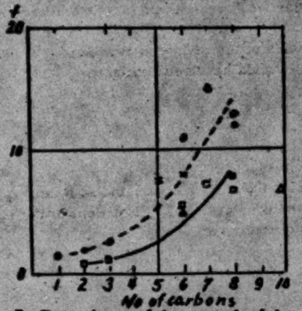


Fig. 7. Dependence of the strength of the oscillator on the structure of the hydrocarbon: ● - saturated aliphatic hydrocarbons (Table 1); x - cycloalkanes; o - aliphatic hydrocarbons having one double bond; Δ - 1,5-hexadiene and dipentene-diprene mixture; □ - isoprene and alloocimene. The broken line is the curve representing the data for saturated hydrocarbons, and the continuous line is for unsaturated hydrocarbons having one double bond. The data for hydrocarbons having 1, 2, and 3 carbons are taken from Friberg's paper [5]

$$f = \frac{B \cdot M}{d} \cdot 1.85 \cdot 10^{-11}, \tag{4}$$

in which d is the density of the substance. Values of f calculated in this way are given in Column 6 of Table 1.

5. Relation between the Constants of the Dispersion Formula and Chemical Structure. Table 1 shows that the values of λ_0 are as follows (in units of 10^{-5} cm):

1) for saturated aliphatic hydrocarbons: methane 1.04, ethane 1.07, propane 1.10, hexane 1.17, heptane 1.14, octane 1.18, 2,2,4-trimethylpentane 1.24;

2) for hydrocarbons having one double bond: ethylene 1.45, propene 1.49, 1-hexene 1.45, 1-heptene 1.40, 1-octene 1.42, 2,2,4-trimethylpentene 1.49;

3) for hydrocarbons having two isolated double bonds: 1,5-hexadiene 1.57, dipentene-diprene mixture 1.57;

4) for hydrocarbons having two conjugated double bonds: isoprene 2.11;

5) for hydrocarbons having three conjugated double bonds: alloocimene 2.69.

These data clearly show the relation existing between the constant λ_0, and the chemical structure of the hydrocarbons.

Table 1 also gives the values of f:

1) for saturated aliphatic hydrocarbons: methane 1.27, ethane 1.94, propane 2.56, hexane 11, heptane 15, octane 13, 2,2,4-trimethylpentane 12;

2) for cycloalkanes: cyclopentane 7.6, methylcyclopentane 7.8;

3) for hydrocarbons having one double bond: ethylene 0.74, propene 0.90, 1-hexene 5.5, 1-heptene 7.3, 1-octene 7.9, 2,2,4-trimethylpentene 6.8.

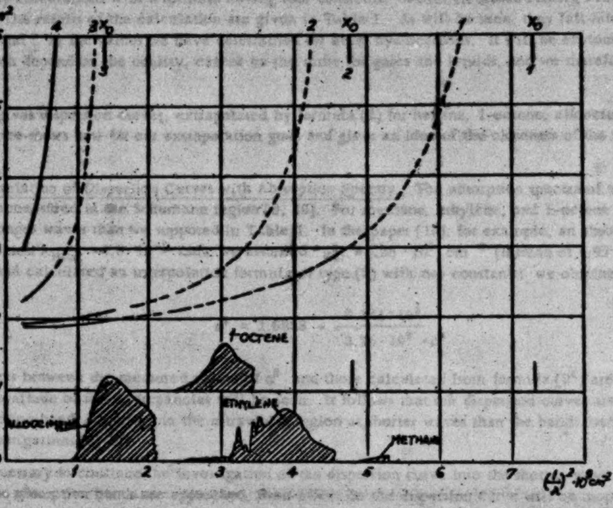


Fig. 8. Dispersion curves: 1) hexane; 2) hexene; 3) alloocimene; 4) anthracene crystal [11]. Values of ν_0^2 from the dispersion curves of the same substances are indicated by X_0 with the numbers 1, 2, 3, and 4. The continous lines are the measured sections of the dispersion curves. The broken lines are the extrapolated parts of the dispersion curves. The lower part of the diagram shows absorption curves for methane [9], ethylene and 1-octene [10], and alloocimene [12]

4) for hydrocarbons having two isolated double bonds: 1,5-hexadiene 4.7, dipentene-diprene mixture 6.5;

5) for hydrocarbons having two conjugated double bonds: isoprene 1.5;

6) for hydrocarbons having three conjugated double bonds: alloocimene 1.8.

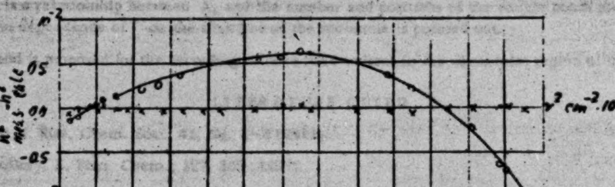


Fig. 9. Comparison with experiment of results for 1-octene obtained from formula (2) by the use of constants from Table 1 (the curve) and obtained from the same formula (2) by the use in it of the value of λ_0 from the paper [10] ($1.8 \cdot 10^{-5}$ cm)

All our values of f are collated in Fig. 7, which gives also the values of f for methane, ethane, propane, butane, and ethylene which we calculated by formula (2) from the experimental values of μ obtained by Friberg [5]. As will be seen, the values calculated from Friberg's data agree very well among themselves; the agreement of our own results is considerably worse, which is clearly to be associated with the fact that Friberg worked with shorter waves. In all cases, however, the effective strengths of the oscillators are colossally high, particularly when it is taken into account that for both D lines of sodium the oscillator strength is unity.

As stated above, Friberg could not find any relationship between the chemical structure and the constants which he obtained by calculations with a formula having four constants. We recalculated Friberg's results according to formula (2). The results of the calculation are given in Table 1. As will be seen, they fall into the same series of values of λ_0 and f as the values we have determined for other hydrocarbons. It will be obvious that the values of A and B, which depend on the density, cannot be the same for gases and liquids, and we therefore do not consider them.

Fig. 8 gives dispersion curves, extrapolated by formula (2) for hexane, 1-octene, alloocimene, and anthracene (C). This figure shows how far our extrapolation goes and gives an idea of the closeness of the agreement that we obtained.

6. Correlation of Dispersion Curves with Absorption Spectra. The absorption spectra of some hydrocarbons have recently been measured in the Schumann region [9, 10]. For methane, ethylene, and 1-octene absorption bands were detected at longer waves than we supposed in Table 1. In the paper [10], for example, an absorption curve for 1-octene is given for which $\lambda_{1\,max} = 1.8 \cdot 10^{-5}$ cm; we assumed $\nu_0^2 = 3.25 \cdot 10^9$ cm^{-2} (instead of $4.97 \cdot 10^9$ cm^{-2}, as given in Table 1) and calculated an interpolation formula of type (3) with two constants; we obtained

$$n^2 = 1.6858 + \frac{9.141 \cdot 10^8}{3.25 \cdot 10^9 - \nu^2} \qquad (2^1)$$

The differences between the measured values of n^2 and those calculated from formula (2^1) are shown in Fig. 9, from which the magnitude of the discrepancies will be seen. It follows that our dispersion curves are determined by more intense absorption bands occurring in the ultraviolet region at shorter waves than the bands found experimentally in the cited investigations [9, 10].

It is necessary to continue the investigation of the dispersion curve into the shorter-wave region of the ultraviolet. As the absorption bands are approached, their effect on the dispersion curve will be more and more pronounced. If we take into account the component of the dispersion curve that is determined by the absorption bands discovered in the investigations [9] and [10], we should be able to fix the positions of the more distant ultraviolet bands with greater accuracy and, with the discovery of these, move further and further into the far ultraviolet and, extrapolating the dispersion curve, find still more new absorption bands.

SUMMARY

1. Dispersion curves were determined for hexane, heptane, 1-octane, 2,2,4-trimethylpentane, cyclopentane, methylcyclopentane, 1,5-hexadiene, a mixture of dipentene and diprene isomers, isoprene, and alloocimene in the wavelength range 6500-2500 A.

2. For all of these hydrocarbons, the constants of a single-term Sellmeier formula were calculated. It was shown that there is a relationship between λ_0 and the number and positions of the double bonds present in the hydrocarbon. The dependence of f on the structure of the molecule is pointed out.

3. A method is proposed for the recording of refractive indices in the ultraviolet region of the spectrum.

LITERATURE CITED

[1] V. Anri, J. Russ. Chem. Soc., 41, No. 1–3 (1919).

[2] H. Voellmy, Z. Phys. Chem., 127, 305 (1927).

[3] C. B. Allsopp, Proc. Roy. Soc. (A) 146 300 (1934).

[4] T. M. Lowry, C. B. Allsopp, Proc. Roy. Soc., 133, 26 (1931).

[5] Sten Friberg, Theses, Lund, 1934.

[6] I. V. Obreimov, Application of Fresnel Diffraction in Physical and Technical Measurements, Acad. Sci. USSR Press, 1945.

[7] I. V. Obreimov and T. N. Shkurina, Bull. Acad. Sci. USSR, Physical Series, 17, 757 (1953).

[8] Robert B. Sosman, The catalogue C$^{2'}$- No. 4 USA, 1927, P. 688.

[9] Philip G. Wilkinson, Herrick L. Johnston, J. Chem. Phys., 18,190, (1950).

[10] J. R. Platt, H. B. Klevens, W. L. Rice, J. Chem. Phys., 17, 466 (1949).

[11] I. V. Obreimov, A. F. Prikhotko, and I. V. Rodnikova, J. Expt. Theor. Phys., 18, 409 (1948).

[12] R. D. Walker, J. Am. Chem. Soc. 74, 4209 (1952).

Received December 4, 1954

N. D. Zelinsky Institute of Organic
Chemistry of the USSR Academy of Sciences

BLANK
PAGE

COMPARATIVE STUDY OF THE OXIDATION REACTIONS OF PECTIC SUBSTANCES, OF CELLULOSE, AND OF THE STRUCTURAL UNITS OF THESE SUBSTANCES

COMMUNICATION 2. OXIDATIVE DEGRADATION OF SODIUM POLYGALACTURONATE BY MEANS OF MOLECULAR OXYGEN, SODIUM METAPERIODATE, AND HYDROGEN PEROXIDE

O. P. Golova and N. S. Mayat

Pectic substances – natural high polymers having chain molecules – are to be found in association with cellulose in almost all plant tissues. It is known that pectic substances can be degraded in a homogeneous medium by various oxidizing agents (chlorine, bromine, periodic acid, hydrogen peroxide, potassium permanganate) with formation of substances of lower molecular weight [1]. However, this matter has not been investigated systematically.

We have studied the oxidative degradation of pectic substances in a homogeneous medium under the action of molecular oxygen, sodium metaperiodate, and hydrogen peroxide: the process was investigated quantitatively, some of the laws governing it were established, and the nature of the oxidative changes in the structural units was determined. As the simplest subject for investigation, we selected polygalacturonic acid, since this forms the skeleton of pectic substances, whatever their origin may be: we prepared it by alkaline hydrolysis of citreous pectin and purified it from accompanying substances (hexosans, pentosans, and carbohydrates containing aldehyde groups). As macromolecular polygalacturonic acid is of low solubility in water, its soluble sodium salt was used for investigation under homogeneous conditions (in aqueous solution).

In our quantitative study of the degradation of sodium polygalacturonate we employed methods based on the viscosity of its sols or solutions and on the determination of the functional groups (aldehyde and carboxyl groups) arising during the oxidation. In all cases the degradation was studied in alkaline solution (pH 12-13). For this reason, electro-viscous phenomena, characteristic of polygalacturonic acid solutions (a heteropolar colloid), were absent. Under these conditions, we were able to characterize the oxidative degradation of sodium polygalacturonate by rate constants calculated from the rate of change of the viscosity of the solution.

We studied the degradation of sodium polygalacturonate by molecular oxygen at various temperature uses and for various concentrations of the reactants. The results enabled us to characterize the degradation reaction by rate constants and temperature coefficient.

Oxidative degradation by molecular oxygen (air) was studied at 20°, about 80°, about 90°, and 135°. The experiments at 20° showed that practically no degradation occurred during the period of time allowed (two hours), the rate constant for the reaction being zero (Table 1 and Fig. 1). Also, there were no changes in the contents of functional groups (Table 2).

When the temperature is raised to 80°, degradation begins to occur at an appreciable rate. With further rise in temperature the rate of degradation rises rapidly, as can be seen from the increase in the value of the rate constant (Table 1 and Fig. 2). At the same time there is an increase also in the number of functional groups (aldehyde and carboxyl groups) (Table 2). On the basis of these results we determined the temperature coefficient for the reaction (1.62).

The effect of the concentration of oxidant (molecular oxygen) on the degradation of sodium polygalacturonate was then studied at a given temperature (95°) (Table 3). Variation of the concentration of oxygen in the reaction medium was effected by variation of its concentration in the gas mixture passed through the solution, the rate of passage (5-6 ml/minute) and the duration of passage (two hours) being maintained constant.

The oxygen concentrations used were 100%, 20% (air), and 0.04% (argon containing oxygen). Oxidation was carried out also at an oxygen concentration that was very close to zero, this being attained by the introduction of an

TABLE 1

Rate Constant (k) for the Degradation of Sodium Polygalacturonate during Oxidation by Molecular Oxygen (Air) and Various Temperatures

Temperature (°C)	$k \cdot 10^3$	Temperature (°C)	$k \cdot 10^3$
20	0	92	7.27
82	4.46	135	47.60

inhibitor (glucose at concentrations of 10% and 20% by weight). The degradation rate constants for these conditions are given in Table 3 and Fig. 3.

The results in Table 3 show that, as would be be expected, change in the concentration of oxidant over a very wide range (100-0.04%) has little effect on the value of the rate constant, the change over this range being only from $10.53 \cdot 10^{-3}$ to $7.87.10^{-3}$. On the other hand, reduction of the concentration of oxidant from 0.04% to almost zero by the introduction of 10% of inhibitor greatly retards oxidative degradation: the rate constant for the degradation reaction is reduced in the ratio of 9.2 : 1 (Table 3 and Fig. 3). Thus, at temperatures in the region of 100° the degradation of sodium polygalacturonate can be brought about by extremely small amounts of molecular oxygen, a result that is in full accord with Golova and Ivanov's results on the effect of very small amounts of oxygen on the oxidative degradation of cellulose in cuprammonium solution [2].

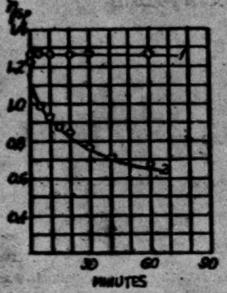


Fig. 1. Degradation of polygalacturonic acid during oxidation by sodium metaperiodate and atomspheric oxygen at 20°: 1 - oxidation by atmospheric oxygen; 2 - oxidation by $NaIO_4$.

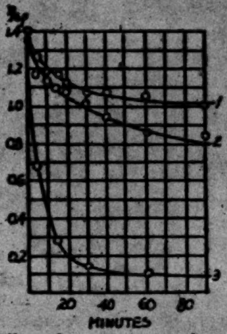


Fig. 2. Effect of temperature on the rate of degradation of polygalacturonic acid during oxidation by atmospheric oxygen: 1 - at 82°; 2 - at 92°; 3 - at 135°.

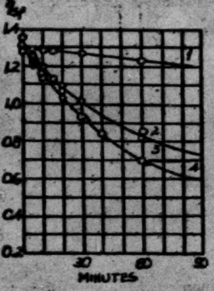


Fig. 3. Effect of the oxygen content of the gas mixture on the degradation of polygalacturonic acid during oxidation by molecular oxygen: 1 - 0%; 2 - 0.04%; 3 - 20%; 4 - 100% of oxygen.

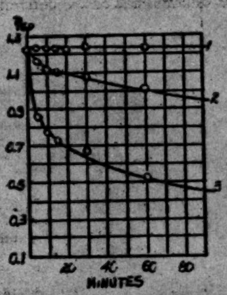


Fig. 4. Degradation of polygalacturonic acid during oxidation by hydrogen peroxide under various conditions: 1 - at 20°; 2 - in presence of a catalyst; 3 - at 95°.

TABLE 2

Contents of Functional Aldehyde and Carboxyl Groups in Polygalacturonic Acid after Oxidation for 30 minutes

Oxidant and oxidation conditions	Number of CHO groups per 1000 repeating units	Number of COOH groups per 1000 repeating units
Atmospheric oxygen at 20°	5.6	811.2
Atmospheric oxygen at 95°	8.4	817.6
Atmospheric oxygen at 135°	21.6	–
Sodium metaperiodate at 20°	12.0	–
Hydrogen peroxide at 20°	6.4	804.8
Hydrogen peroxide at 95°	16.8	832.0
Hydrogen peroxide at 20° in presence of a catalyst	11.4	802.4
Unoxidized material	6.0	800.0

TABLE 3

Rate Constants for the Degradation of Sodium Polygalacturonate during Oxidation by Molecular Oxygen at 95° for Varying Concentrations of Oxygen in the Gas Phase.

Oxygen content of gas phase (%)	$k \cdot 10^3$
~100	10.53
~20	8.50
~0.04	7.87
~0	0.85

TABLE 4

Rate Constants for the Degradation of Sodium Polygalacturonate during Oxidation by Sodium Metaperiodate and Hydrogen Peroxide under Various Conditions.

Oxidant and conditions of oxidation	$k \cdot 10^3$
Sodium metaperiodate at 20°	16.20
Hydrogen peroxide at 20°	0
Hydrogen peroxide at 95°	10.84
Hydrogen peroxide at 20° in presence of a catalyst	4.60

Our results enabled us to make an approach to an explanation of the mechanism of the oxidative degradation. On the basis of these results, it may be supposed that the primary cause of the degradation of sodium polygalacturonate in an alkaline medium at temperatures in the region of 100° is not the hydrolysis of the glucoside link under the influence of the carboxyl group standing at C-6, but the conversion of hydroxyls on C-1, C-2, and C-3 into other functional groups, with the result that the glucoside link is weakened and undergoes hydrolysis in an alkaline medium. It is known that such groups may be aldehyde and ketone groups, and also carbonic ester groupings [3, 4]. It is in fact found that practically no degradation of polygalacturonic acid is produced at 20° by molecular oxygen, this being associated with the absence of the formation of functional groups.

With increase in temperature the rate of degradation increases and there is an accompanying formation of new functional groups (aldehyde and carboxyl groups). This can be seen more clearly from the example of the degradation of polygalacturonic acid by sodium metaperiodate, for it is known that sodium metaperiodate breaks the bond between C-2 and C-3 in the structural units of cellulose and polygalacturonic acid with formation of two aldehyde groups [5].

The degradation of sodium polygalacturonate by sodium metaperiodate was studied in an alkaline medium at 20°. The concentration of oxidant was equivalent to 0.5 g/liter of active oxygen in the solution. The results – rate constant for the degradation reaction (Table 4 and Fig. 1) and aldehyde contents of the oxidation products (Table 2) – show that oxidation by sodium metaperiodate results in rapid degradation of polygalacturonic acid accompanied by rapid increase in the number of aldehyde groups.

These results confirm that the degradation of sodium polygalacturonate, not only by sodium metaperiodate but also by molecular oxygen, results from the oxidation of hydroxyls with formation of new functional groups (aldehyde groups) that reduce the stability of the glucoside link in an alkaline medium. It should be noted that the increase in the content of aldehyde groups during oxidation by molecular oxygen or sodium metaperiodate is considerably greater than the increase that could occur under these conditions as the result of the hydrolysis of the glucoside links of the polymer in an alkaline medium. The same is found in oxidation by hydrogen peroxide.

Unlike sodium metaperiodate, hydrogen peroxide, in oxidizing the hydroxyls at C-2 and C-3 of the structural unit of cellulose, yields not only aldehyde, but also ketone groups [4]. Like aldehyde groups, such ketone groups reduce the stability of the glucoside link in an alkaline medium and facilitate its rupture.

The degradation of sodium polygalacturonate by hydrogen peroxide was studied at 20° and 95°, and also at 20° in presence of a catalyst. The results (Tables 2 and 4, Fig. 4) show that at 20° the sodium salt is as stable to hydrogen peroxide as it is to molecular oxygen. Rise in temperature to 95° or introduction of a catalyst brings about degradation at a rate depending on the conditions.

EXPERIMENTAL

Preparation of Polygalacturonic Acid from the Inner Skin (Albedo) of Citreous Fruits

1. Isolation of Pectin from Albedo. The albedo was removed from a fresh orange, ground, and extracted with water at 30° for 24 hours. The extract was filtered and poured into twice its volume of alcohol. The precipitated white mass of pectin was filtered off, pressed off, and dissolved in a little water. It was then reprecipitated with alcohol, filtered off, washed with alcohol and ether, and dried in the air.

2. Preparation of Polygalacturonic Acid by the Alkaline Hydrolysis of Pectin. The pectin (10 g) was dissolved with stirring in 1 liter of 0.1 N NaOH at room temperature. The temperature was raised slowly to 40°, and the solution was then filtered and poured slowly into excess of hydrochloric acid. The precipitated pectic acid was filtered off, washed with alcohol until the reaction for chloride was negative, washed further with ether, and dried in the air.

3. Purification of Polygalacturonic Acid from Reducing and Coloring Matters. The polygalacturonic acid was treated with an acid solution (pH 3-4) of sodium chlorite (0.1 N) for 20 hours at room temperature. The acid was then filtered off, washed with 60% alcohol until reaction for chloride was negative, washed further with ether, and dried to constant weight over phosphoric oxide in a vacuum desiccator. The polygalacturonic acid obtained in this way was found to contain 0.05% of aldehyde groups, 0.02% of methoxyl groups, and 20.04% of carboxyl groups. Further purification did not result in increase in carboxyl content.

Preparation of Solutions of Sodium Polygalacturonate in 0.05 N NaOH

In order to prepare 0.5% solutions of sodium polygalacturonate, an accurately weighed 0.450-g sample of polygalacturonic acid was dissolved in an equivalent amount of 0.1 N NaOH. The solution was filtered through a No. 2 glass filter and transferred to a 100-ml measuring flask; a further 50 ml of 0.1 N NaOH was added, and the solution was made up to the mark with water. Solutions of lower concentration (0.25% and 0.125%) were prepared by the same method, but the amounts of acid and alkali taken were correspondingly reduced.

Determination of the Viscosities of Solutions of Sodium Polygalacturonate in an Alkaline Medium

Ten milliliters of a solution of the salt prepared as indicated above was transferred to an Ostwald viscometer contained in a 20° thermostat. The solution was maintained at this temperature in the viscometer for 2-3 minutes, and the time of efflux of the solution was then determined. The determination was repeated three times. The time of efflux was determined in the same way for the solvent, i.e. 0.05 N NaOH. The specific viscosity was calculated by the formula $\eta_{sp} = (t - t_0)/t_0$, in which η_{sp} is the specific viscosity, $\underline{t}$ is the time of efflux of the solution seconds, and t_0 is the time of efflux of the solvent (seconds).

Degradation of Sodium Polygalacturonate during Oxidation by Molecular Oxygen, Sodium Metaperiodate, and Hydrogen Peroxide

Oxidation by Molecular Oxygen. The 0.5% solution of the sodium salt prepared as indicated above was poured into a Drechsel bottle. The bottle was placed in a thermostat at the required temperature and connected, on the one side through a small bottle containing the same solution to a gas meter and, on the other, to a Mariotte bottle. When the required temperature was attained in the solution, the heated gas was passed at 5-6 ml/minute. Oxidation was continued for three hours, the volume of gas passed during this period being about 1 liter.

After 5, 10, 15, 20, 30, 60, 120, and 180 minutes from the commencement of oxidation, passage of oxygen was interrupted and 10 ml of the solution was transferred by pipet to a bottle having a ground-in stopper. The solution was cooled rapidly and transferred to an Ostwald viscometer; its specific viscosity was then determined as described above. In this way oxidation with molecular oxygen was carried out at different concentrations in the gas mixture: ~100%, ~20% (air), 0.04%, and ~0%. In the oxidation with molecular oxygen (air) in presence of glucose, the concentration of the latter in the solution was 10% by weight; in other respects the experimental procedure remained the same.

Oxidation by Molecular Oxygen (Air) under Pressure. The 0.5% solution of sodium polygalacturonate prepared as indicated above was introduced in 11-12-ml portions into 15-20-ml ampoules, which were sealed and placed in a thermostat at 135-140°. After 5, 10, 15, 20, 30, 40, 60, 120, and 180 minutes from the commencement of oxidation (the commencement was taken to be the moment at which a temperature of 135° was attained), ampoules were taken from the thermostat, rapidly cooled in ice water, and opened. The solution was transferred to an Ostwald viscometer, and its specific viscosity was determined.

Oxidation by Sodium Metaperiodate. Ten milliliters of a 0.5% solution of sodium polygalacturonate was transferred by pipet to a viscometer contained in a 20° thermostat, and the calculated amount of a saturated solution of sodium metaperiodate was added. The contents of the viscometer were mixed rapidly, and the time of mixing was taken to be the time of the commencement of oxidation. After 5, 10, 15, 20, 30, 60, 120, and 180 minutes from the commencement, the specific viscosity was determined. Parallel determinations were made on the solutions before oxidation, a volume of distilled water equal to the volume of metaperiodate introduced being added to 10 ml of the solution.

Oxidation by Hydrogen Peroxide. A 0.5% solution (100 ml) of sodium polygalacturonate was introduced into a round-bottomed flask fitted with reflux condenser, and the flask was placed in a thermostat at the required temperature. Oxidation was considered to begin when the maximum temperature was attained in the solution (92°). After 5, 10, 15, 20, 30, 40, 60, 120, and 180 minutes from the commencement of oxidation, 10 ml of solution was removed by pipet, cooled, and transferred to a viscometer.

Separation of Oxidized Preparations of Polygalacturonic Acid from Solutions of the Sodium Salts After being oxidized for 30 minutes, the solution of the sodium salt was cooled with ice water and poured into excess of 0.1 N HCl. The voluminous precipitate of polygalacturonic acid was filtered off, washed with hydrochloric acid, pressed off, and then allowed to stand overnight in 0.1 n HCl to complete demineralization. It was then filtered off, washed with 60% alcohol until reaction for chloride was negative, then washed with 96% alcohol and with ether, and dried over phosphoric oxide to constant weight.

SUMMARY

1. When molecular oxygen, sodium metaperiodate, and hydrogen peroxide react with sodium polygalacturonate, oxidative degradation may occur at a rate that depends both on the identity of the oxidant and on the oxidation conditions (temperature, concentration of oxidant, presence of catalyst).

2. The cause of the degradation of sodium polygalacturonate under these conditions is the formation of new functional groups, which brings about rupture of glucoside links in an alkaline medium. An essential condition for degradation is the use of oxidizing agents that act preferentially on the hydroxyls at C-2 and C-3.

3. The oxidation of C-2 and C-3 hydroxyls can be effected not only by the specific oxidant, sodium metaperiodate, but also by molecular oxygen and by hydrogen peroxide at temperatures in the region of 100°, and also by hydrogen peroxide in presence of a catalyst at room temperature.

LITERATURE CITED

[1] H. Pallman, H. Deuel, Experientia 1, 89 (1945); A. Scheele, Chimia 1, 33 (1947); H. Deuel, Helv. 26, 2002 (1943); A. G. Norman, F. W. Norris, Biochem. Z. 2, 402 (1930).

[2] O. P. Golova, V. I. Ivanov, and N. I. Nikolaeva, Proc. Acad. Sci. USSR, 58, No. 4, 599 (1947).

[3] V. I. Ivanov and E. D. Kaverzneva, Prog. Chem., 13, No. 4, 281 (1944).

[4] V. I. Ivanov, E. D. Kaverzneva, and Z. I. Kuznetsova, Proc. Acad. Sci. USSR, 86, No. 2, 301 (1952); Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, No. 2, 374 (T.p. 341)*.

Received December 7, 1954

Forestry Institute of the USSR Academy
of Sciences

---

* T.p. = C. B. Translation pagination.

SYNTHESIS OF SULFUR COMPOUNDS BY THE AID OF VINYL ETHERS AND ACETYLENE

COMMUNICATION 13. GENERAL METHOD FOR THE SYNTHESIS OF VINYL SULFIDES

M. F. Shostakovsky, E. N. Prilezhaeva, and N. I. Uvarova

Few simple accessible methods have been reported for the preparation of unsaturated sulfur compounds which, on account of the presence of reactive double bonds in their molecules, could be used in the synthesis of various new substances. We now report a general method of the synthesis of one class of such substances – vinyl sulfides. The method is based on the vinylation of thiols as already applied by us for the preparation of ethyl vinyl sulfide [1, 2] and a series of alkoxyethyl vinyl sulfides [3]:

$$RSH + CH \equiv CH \xrightarrow[135\text{-}145^\circ]{5\%\,KOH} RSCH = CH_2 \qquad (1)$$

We showed [1, 2, 3] that a good yield of the vinyl sulfide can be obtained only in presence of an excess of acetylene, which, to a considerable extent, suppresses the secondary reaction in which a 1,2-bis (alkylthio) ethane is formed:

$$RSH + RSCH = CH_2 \rightarrow RSCH_2CH_2SR. \qquad (2)$$

In an attempt to extend the reaction conditions that we had established to reaction between acetylene and other thiols we discovered that, depending on the structure of the thiol, it was necessary to make considerable changes in such parameters of the process as temperature and catalyst concentration and also to introduce solvents and diluents. For example, at 135-150° in presence of caustic potash and excess of acetylene, 1-butane-, 1-propane-, 3-methyl-1-butane-, and α-toluene-thiols were completely resinified. This behavior is probably associated with the thermal instability of these compounds [4]. The use of solvents such as benzene, toluene, and ethanol and lowering of the vinylation temperature to 100-110° without introduction of solvent did not give the desired results. We than tried the use of water as a diluent, since it is known to reduce resinification considerably in the synthesis of aryl vinyl ethers [5]. We lowered the reaction temperature to 70-90° and diluted the reaction mixture (which contained 10 mole-% of KOH) with water; we were then able to synthesize butyl vinyl sulfide in about 30% yield. However, in this case the best results were obtained by the use as solvent of dioxane, which can dissolve considerable amounts of acetylene under pressure. This property of dioxane makes it easy to create a large excess of acetylene (2.5-3 moles per mole of thiol)* during the vinylation. Treatment of 1-butanethiol under these conditions (at 70-90°) yielded butyl vinyl sulfide in 70% yield. The actual yield of butyl vinyl sulfide was somewhat higher, since some losses evidently occurred as a result of the necessity of washing the reaction products with water to remove dioxane.

Under the same conditions other aliphatic vinyl sulfides were prepared in 65-75% yield, i.e. propyl vinyl sulfide, isopentyl vinyl sulfide, and the aralkyl sulfide benzyl vinyl sulfide. A somewhat lower yield was obtained in the vinylation of benzenethiol (50% in a dioxane medium and 70-72% in a butanol medium).

The method that we have proposed – which is based on the reaction of thiols with acetylene indiluted with inert gases and is a further development of Favorsky and Shostakovsky's reaction – permits us, therefore, to synthesize vinyl sulfides of any structure. In this respect the method differs essentially from the patented method of vinylating mercaptans with an acetylene-nitrogen mixture [7], which gives good yields only for aryl vinyl sulfides.

---

* This property of dioxane has already been applied by two of us in collaboration with Tsymbal for the preparation of the tetravinyl ether of methyl glucoside [6].

TABLE 1

Physical Properties of Vinyl Sulfides *

No.	R	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	MR		Yield (%)
					Found	Calculated	
1	C_2H_5	91.9-92.2 (760)	0.8767	1.4756	28.37	28.12	61.0
2	n-C_3H_7	43.5 (50)	0.8723	1.4734	32.89	32.86	60.0
3	n-C_4H_9	47.5-48.5 (24)	0.8698	1.4722	37.47	37.48	70.0
4	i-C_5H_{11}	53.5-54.5 (17)	0.8615	1.4704	42.21	42.09	65.0
5	$C_6H_5CH_2$	90-90.5(7)	1.0347	1.5794	48.28	47.73	76.2
6	C_6H_5	76.5 (4)	1.0417	1.5888	44.05	43.12	71.6

---

* For vinyl sulfides the literature gives: No. 4 b.p. 30-32° (4 mm); n_D^{20} 1.4715; d_4^{20} 0.8656 [8]; No. 5 b.p. 73° (3 mm) [7]; No. 6 b.p. 200-201°; n_D^{20} 1.5883 [9]; b.p. 76-78° (4 mm) [10].

TABLE 2

Comparison of the Boiling Points of alcohols ROH and thiols RSH with those of Vinyl Ethers $ROCH{=}CH_2$ and Vinyl Sulfides $RSCH{=}CH_2$ Snythesized from them

No.	R	B.p. (°C at 760 mm)		Δt (°C)	B.p. of thiol (°C at 760 mm)	B.p. of vinyl sulfide in °C (p in mm)	Δt (°C)
		of alcbhol	of vinyl ether				
1	C_2H_5	78.0	36.0	−42.0	34.4-34.6	91.9-92.2 (760)	+57.5
2	n-C_3H_7	97.0	65.0	−32.0	67.4-67.6	43.5 (50)	~+ 50.0
3	n-C_4H_9	117.0	93.8	−23.2	98.6-99	144.0 (760)*	+45.0
4	i-C_5H_{11}	131.1-131.4	112.5-112.7	−18.6	120.1	54 (17)	~+40
5	C_6H_5	182.3-182.5	155-156	−27.3	166-169	200-201 (760)	+32
6	$C_6H_5CH_2$	205.3	183-184	−22.3	194-195	90-90.5 (7)	+30-40

---

* with decompostion

TABLE 3

Physical Properties of 1,2-Bis(alkylthio) - and 1,2-Bis(arylthio)-ethanes *

No.	$RSCH_2CH_2SR'$	B.p.in °C (p in mm)	n_D^{20}	d_4^{20}	MR	
					Found	Calculated
1	$C_3H_7SCH_2CH_2SC_3H_7$	91-92.5 (3)	1.5046	0.9565	55.27	55.08
2	$C_4H_9SCH_2CH_2SC\ H_9$	131-132 (6)	1.4967	0.9355	64.53	64.32
3	$C_4H_9SCH_2CH_2SC_2H_5$	98.5 (3.5)	1.5013	0.9539	55.08	55.08
4	$C_4H_9SCH_2CH_2SCH_2CH_2OC_4H_9$	155 (4)	1.4900	0.9600	75.42	75.20
5	$C_6H_5SCH_2CH_2SC_6H_5$	67.5 (m.p.)	–	–	–	–

---

* No. 1 and 2 were obtained by the vinylation of thiols, and No. 3, 4, and 5 were prepared by simple mixture of thiol and sulfide in the open. The literature gives: for No. 2 b.p. 129-130° (5 mm); d_4^{20} 0.3989; n_D^{20} 1.4962 [20]; and for No. 5 b.p. 69° [7].

Vinyl sulfides are volatile substances of unpleasant odor. They are insoluble in water, but tend to attract moisture, from which it is difficult to free them. Vinyl sulfides are best preserved in sealed ampoules from which air has been displaced by dry nitrogen, and these should be kept in the dark, since, under the action of light – particularly in the presence of oxygen – the vinyl sulfides tend to polymerize. Table 1 gives the physical properties of the vinyl sulfides that we have synthesized, including the previously described ethyl vinyl sulfide [1, 2].

It will be seen from Table 1 that for the aliphatic vinyl sulfides the exaltation of molecular refraction is not great –0.1-0.25 on the average – which indicates that the interaction between the electrons of the double bond and of the sulfur atom is low *.

---

* In the calculation of molecular refraction, the value of the atomic refraction of sulfur found for diallyl sulfide (8.04) was used [11].

TABLE 4

Synthesis of Butyl Vinyl Sulfide

Expt. No.	Amount taken					Reaction conditions*		Yield of reaction products (%)	
	of 1-butanethiol (g)	of acetylene (moles per mole of thiol)	of KOH (mole-%)	Of solvent		Temperature (°C)	Duration of heating hours	Butyl vinyl sulfide	1,2-Bis(butylthio)ethane
				Name of solvent	Amount (g)				
1	7.0	1.6	8	–	–	150-160	1.5	–	–
2	7.0	1.6	8	Benzene	7.0	135-145	1.5	–	–
3	6.2	1.9	5	Ethanol	6.0	160-170	1.5	–	–
4	8.5	1.4	5	Toluene	15.0	155-165	2.0	–	–
5	8.0	1.2	10	–	–	100-110	1.5	–	–
6	8.0	1.2	10	Water	8.0	70-90	1.5	30.0	–
7	25.0	1.2	100	Water	55.0	70-90	3.0	30.0	14.0
8	30.0	2.4	20	Dioxane	45.0	70-90	1.0	62.0	9.0
9	106.5	3.1	20	Dioxane	180.0	70-90	1.0	70.0	6.5

*The capacities of the autoclaves used were as follows: Experiments 1-6, 150 ml; Experiments 7 and 8, 500 ml; and Experiment 9, 2500 ml. In Experiments 1, 3, 4, and 5 only resin was isolated, but in Experiment 2 some unchanged thiol was present, in addition to resin.

TABLE 5

Synthesis of Propyl, Isopentyl, Benzyl, and Phenyl Vinyl Sulfides $RSCH=CH_2$

R	Expt. No.	Amount taken					Reaction conditions*		Yield of reaction products (%)	
		of thiol (g)	of acetylene (moles per mole of thiol)	of KOH (mole-%)	Of solvent		Temperature (°C)	Duration of heating hours	Vinyl sulfide	1,2-Bis(alkylthio)ethane
					Name of solvent	Amount (g)				
C_3H_7	1	6.0	1.8	10	–	–	135-150	1.0	–	–
	2	20.0	2.5	20	Dioxane	35	70-90	1.0	60.0	8.5
i-C_5H_{11}	1	8.0	1.8	10	–	–	140-150	1.0	–	–
	2	27.0	2.5	20	Dioxane	45	70-90	1.0	65	–
$C_6H_5CH_2$	1	8.5	1.6	5	–	–	150-170	1.5	–	–
	2	8.0	2.6	20	Dioxane	15	70-90	1.0	76	–
C_6H_5	1	10.0	1.4	5	–	–	160-180	1.5	36.6	–
	2	30.0	1.4	5	–	–	160-180	1.5	40.0	–
	3	22.0	1.5	10	Water	5	160-180	2.5	40.7	–
	4	30.0	1.4	10	Butanol	30	145-160	3.0	71.6	–
	5	30.0	2.0	20	Dioxane	45	90-110	1.0	50.0	–

For the quantitative analysis of the vinyl sulfides and the determination of their purity we used the cleavage reaction with excess of alcoholic mercuric chloride, already described in various papers [2, 3]:

$$RSCH{=}CH_2 + HgCl_2 + 2\,C_2H_5OH \rightarrow RSHgCl + HCl + CH_3CH(OC_2H_5)_2 \qquad (3)$$

In Table 2 comparisons are made between the boiling points of thiols [15-18] and the vinyl sulfides synthesized from them on the one hand and the boiling points of alcohols and the corresponding vinyl ethers on the other [12-14]. Vinyl ethers boil considerably lower than the original alcohols, since the boiling points of the latter are abnormally high as a result of association and do not correspond to their molecular weights. It is known that association between sulfur atoms by hydrogen bonding is not possible, so that in the series of thiols and sulfides the normal correspondence between boiling point and molecular weight is to be observed.

As already stated, the formation of vinyl sulfides is complicated by the secondary reaction in which 1,2-bis (alkylthio) ethanes are formed. These substances can readily be obtained as sole reaction product, and they may be prepared by direct reaction between thiols and the vinly sulfides in the air. This confirms the tendency of vinyl sulfides to undergo free-radical reactions which we have pointed out previously. Under the same conditions vinyl ethers give a mixture of addition products formed in accordance with and contrary to Markovnikov's rule [19]. In Table 3 we give the physical properties of the 1,2-bis (alkylthio)- and 1,2-bis (arylthio)-ethanes that we have synthesized.

EXPERIMENTAL

I. Synthesis of Vinyl Sulfides

The vinyl sulfides were synthesized in rotating autoclaves provided with heaters. The thiols were freshly distilled. The dioxane that was used in some of the experiments was purified by Hess and Frahm's method [21] and gave a negative reaction with pure mercury for the presence of the peroxide.

a) Synthesis of Butyl Vinyl Sulfide. The different variants tried for the synthesis of butyl vinyl sulfide are indicated in Table 4. One of the experiments is described by way of example.

Experiment 9. A mixture of 106.5 g of 1-butanethiol, 180.0 g of dioxane, and 13.2 g of KOH (20 mole-%) was prepared in an autoclave. The reaction mixture was completely saturated with acetylene in the cold, for which purpose it was passed into the autoclave in three doses, each followed by agitation for 10-15 minutes*. In this way for each mole of thiol 3.1 moles of acetylene was introduced, of which 1.5 moles was in the gas phase and 1.6 moles in the dissolved condition. The temperature was maintained at 70-90° for one hour, and the maximum pressure attained was 30 atm. Ether (250 ml) was added to the reaction mixture, and the ether extract was washed with water (4-5 300-ml portions). The ether extract was dried over sodium sulfate (it is necessary to dry it for at least one day).

Ether was removed, and vacuum distillation then yielded the following fractions:

Fraction I, B.p. 35-50 (20 mm); 4.0 g; n_D^{20} 1.4705
Fraction II B.p. 50.5-51,5(20 mm); 96.0 g; n_D^{20} 1.4720
Fraction III B.p. 60-137 (6 mm); 1.5g; n_D^{20} 1.4850
Fraction IV B.p. 137-140 (6 mm) 8.5g; n_D^{20} 1.4965
Resinous residue 0.5 g

After refractionation, butyl vinyl sulfide (Fraction II) had b.p. 47.5-48.5° (21 mm); n_D^{20} 1.4722; d_4^{20} 0.8698; Calculated MR 37.48; Found MR 37.47.

Found %: C 62.10; 61.77; H 10.53; 10.52; S 27.64; 27.68
$C_6H_{12}S$. Calculated %: C 62.00; H 10.41; S 27.59

The content of butyl vinyl sulfide, determined by the mercuric chloride method [2,3], was 98.3 - 99.1%.

Fraction IV was 1,2-bis (butylthio) ethane, obtained in 7.5% yield; its constants were close to those given in the literature [20] (see Tabel 3).

Found % C 58.25; 58.29; H 10.79; 10.81; S 30.96; 31.12
$C_{10}H_{22}S_2$. Calculated % C 58.19; H 10.79; S 31.07

---

* In order to obtain the necessary excess of acetylene it is essential to use cylinders containing acetylene at not less than 15 atm (better, 17-18 atm).

TABLE 6

Analytical Results

Formula of substance	Combustion analysis [24]						Analysis by the mercuric chloride method [2, 3] %
	Found in %			Calculated in %			
	C	H	S	C	H	S	
$CH_2{=}CHSC_3H_7$	–	–	31.42.50	–	–	31.37	99.4-99.5
$C_3H_7SCH_2CH_2SC_3H_7$	54.18	9.98	35.70	53.87	10.17	35.95	–
	54.00	9.88	35.76				
$CH_2{=}CHSC_5H_{11}$ (-i)	–	–	–	–	–	–	99.4-99.5
$CH_2{=}CHSCH_2C_6H_5$	71.92	6.72	21.38	71.95	6.71	21.34	97.2-97.9
	72.08	6.77	21.31				
$CH_2{=}CHSC_6H_5$	70.74	5.96	23.53	70.53	5.92	23.54	99.5-100
	70.78	6.01	23.28				

TABLE 7

Synthesis of 1,2-Bis(alkylthio)- and 1,2-Bis (arylthio)-ethanes

Expt. No.	Amount of vinyl sulfide taken		Amount of thiol taken		Yield bis-ethanes (%)	Analytical results					
						Found in %			Calculated in %		
	Formula	Amount (g)	Formula	Amount (g)		C	H	S	C	H	S
1	$CH_2{=}CHSC_4H_9$	5.8	C_2H_5SH	4.5	100.0	53.88	10.27	35.89	53.87	10.17	35.96
			$CH_2OC_4H_9$•			54.17	10.04	35.95			
2	$CH_2{=}CHSC_4H_9$	5.8	|	10.0	90.0	57.56	10.46	24.41	57.55	10.46	25.60
			CH_2SH			57.75	10.37	25.70			
3	$CH_2{=}CHSC_6H_5$••	0.8	C_6H_5SH	1.0	100.0	–	–	–	–	–	–

• 2-Butoxyethanethiol was synthesized by the action of hydrogen sulfide on butyl vinyl ether [25].

•• The reaction product was not analyzed since its melting point was identical with that given in the literature (see Table 3).

This substance is 1,2-bis (butylthio) ethane, not 1,1-bis(butylthio)-ethane, for it does not give a pink color when an excess of alcoholic mercuric chloride is added in presence of Methyl orange [19].

In Experiment 7 (see Table 4), in which the 1-butanethiol to be vinylated was completely converted into mercaptide, not only butyl vinyl sulfide and 1,2-bis (butylthio) ethane were isolated, but also dibutyl sulfide, b.p. 54° (4 mm) and n_D^{20} 1.4548, was obtained in 12.5% yield. The salt formed by dibutyl sulfide with mercuric chloride melted at 111-112°. The literature gives $(C_4H_9)_2S$, b.p. 182° [22] and $(C_4H_9)_2S \cdot 2HgCl_2$, m.p. 111-112° [23].

b) The Conditions for the Synthesis of Other Vinyl Sulfides are summarized in Table 5; their physical properties are given in Table 1, and analytical data are given in Table 6.

Propyl and butyl vinyl sulfides have not been described in the literature. Isopentyl vinyl sulfide was prepared by Khomenko [8] in 45% yield [together with diisopentyl sulfide and 1,2-bis (isopentylthio)-ethane] by the action of acetylene on an aqueous solution of 3-methyl-1-butanethiol. The preparation of benzyl vinyl sulfide (without indication of the yield) and of phenyl vinyl sulfide (in 90% yield) by the action of an acetylene-nitrogen mixture on thiols is described in German patents [7]: Phenyl vinyl sulfide has been prepared also by the decomposition of dimethylphenyl (2-phenylthioethyl)- ammonium iodide [9] and by the pyrolysis of 1,2-bis (phenylthio) ethane [10].

II. Synthesis of 1,2-Bis (alkylthio)- and 1,2-Bis (arylthio)-ethanes

1,2-Bis (alkylthio)- and 1,2-bis (arylthio)-ethanes were prepared by mixing the corresponding thiols and sulfides in the open. After 5-10 minutes the mixture began to grow warm. When the thiol had a low boiling point, the temperature of the mixture was maintained at not above 20-25° by the aid of ice water. When high-boiling thiols were used, the mixture was not cooled and the temperature rose to 70-80°. On the next day the reaction mixture was fractionated (Experiments 1 and 2). None of the synthesized substances gave an acid reaction to Methyl orange after addition of excess of alcoholic mercuric chloride, i.e., they were free from the isomeric mercaptals. The physical constants of these bis (alkylthio)- and bis (arylthio)-ethanes are given in Table 3, and the experimental conditions and analytical results are given in Table 7.

SUMMARY

1. A general method based on the Favorsky-Shostakovsky reaction was developed for the synthesis of vinyl slufides of various structures. The essence of the method is reaction between thiols and excess of acetylene, undiluted by inert gas, in presence of caustic potash.

2. It was shown that, even under optimum vinylation conditions, a secondary process occurs with formation of bis (alkylthio)- and bis (arylthio)-ethanes. The latter substances can be prepared in theoretical yield by simply mixing vinyl sulfides with thiols in the open. This reaction indicates the great tendency of vinyl sulfides to undergo free-radical transformations.

3. It was shown that the cleavage of vinyl sulfides with excess of alcoholic mercuric chloride is quantitative and can be used for the titration of all vinyl sulfides.

LITERATURE CITED

[1] E. N. Prilezhaeva and M. F. Shostakovsky, Syntheses of Organic Compounds, Collection 2, Acad. Sci. USSR Press, Moscow, 1952, p. 54.

[2] M. F. Shostakovsky, E. N. Prilezhaeva, and N. I. Uvarova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 3, 526. (T.p. 447)*.

[3] E. N. Prilezhaeva and M. F. Shostakovsky, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 3, 517 (T.p. 439)*.

[4] M. G. Rudenko and V. N. Gromova, Proc. Acad. Sci. USSR, 81, 207 (1951).

[5] M. F. Shostakovsky and M. S. Burmistrova, J. Appl. Chem., 15, 260 (1942).

[6] M. F. Shostakovsky, E. N. Prilezhaeva, and L. V. Tsymbal, Proc. Acad. Sci. USSR, 96, 99 (1954).

[7] J. W. Copenhaver, Acetylene and Carbon Monoxide Chemistry, 1949, p. 88; C. E. Schildknecht, Vinyl and Related Polymers, 1952, p. 635; W. Reppe, H. Ufer, E. Kühn, U. S. Patent 2125649, 1938; C. A. 32, 7, 615 (1938).

[8] A. Kh. Khomenko, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1951, No. 3, 280.

[9] J. Braun, G. Kirschbaum, Ber. 53, 1399 (1920).

[10] E. F. Landau, U.S. Patent 2,490,875, 1949; C. A. 44, 4502 (1950); British Pat. 660054, 1951; C. A. 46, 9126 (1952).

[11] T. S. Price, D. T. Twiss, J. Chem. Soc. 101, 1259 (1912).

[12] M. F. Shostakovsky, Vinyl Ethers, Acad. Sci. USSR Press, Moscow, 1952.

[13] A. Landau, Ber. 7, 1687 (1874).

[14] W. Louginine, Ann. Chem. Phys. 7, 13, 330 (1898).

[15] L. M. Ellis, E. E. Reid, J. Am. Chem. Soc. 54, 1674 (1932).

[16] Ballard, Ann. 52, 313 (1844).

[17] Organic Syntheses, Collected Volume 1 (edited by H. Gilman; Russian translation), Foreign Lit. Press, Moscow, 1949, p. 381.

[18] V. M. Rodionov and N. N. Suvorov, Syntheses of Organic Compounds, Collection 1, Acad. Sci. USSR Press, Moscow 1950, p. 10.

[19] M. F. Shostakovsky, E. N. Prilezhaeva, and E. S. Shapiro, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, No. 2, 357, (T.p. 325)*.

[20] T. C. Wither, E. E. Reid, J. Am. Chem. Soc. 43, 639 (1920).

[21] R. Hess, H. Frahm, Ber. 71, 2629 (1938).

[22] N. Grabovsky and A. Zaitsev, 171, 253 (1874).

[23] W. F. Faragher, J. C. Morell, S. Comey, J. Am. Chem. Soc. 51, 2774, 81, (1929).

[24] M. G. Korshun and N. S. Sheveleva, J. Anal. Chem. 7, 104 (1952) (T.p. 121)*

[25] M. F. Shostakovsky, E. N. Prilezhaeva, and E. S. Shapiro, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 2, 292 (T.p. 236)*.

Received October 20, 1954

N. D. Zelinsky Institute of Organic
Chemistry of the USSR Academy of Sciences

* T.p. = C. B. Translation pagination

BLANK
PAGE

SYNTHESIS AND REACTIONS OF VINYL ETHERS OF ETHANOLAMINES

COMMUNICATION 7. VINYL ETHER OF 2-DIPHENYLAMINOETHANOL

M. F. Shostakovsky and I. A. Chekulaeva

Study of the properties of some vinyl ethers of ethanolamines has shown that the vinyl ethers of monoethanolamine $CH_2{=}CHOCH_2CH_2NH_2$ (I) and diethanolamine $(CH_2{=}CHOCH_2CH_2)_2NH$ (II) and $CH_2{=}CHOCH_2CH_2NHCH_2CH_2OH$ (III) are distinguished by chemical inertness in reactions characteristic for alkyl vinyl ethers, which occur in presence of ionogenic catalysts [1, 2]. This behavior is associated with the presence in their molecules of nitrogen and oxygen, which are capable of forming onium compounds, and with the presence also of a hydrogen bond of the type –N–H···O– [3].

The effect of a hydrogen bond is excluded in those vinyl ethers of ethanolamines which contain a tertiary amino group. It is in fact found that the vinyl ether of 2-diethylaminoethanol $CH_2{=}CHOCH_2CH_2N(C_2H_5)_2$ (IV), unlike the vinyl ethers (I), (II), and (III), reacts with alcohols. The effect of the presence of a nitrogen capable of forming onium compounds is still felt, however, and for the vinyl ether of 2-diethylaminoethanol acetal formation occurs under more severe conditions and in lower yield than for unsubstituted alkyl vinyl ethers. No polymerization at all will occur in presence of ionic catalysts [1].

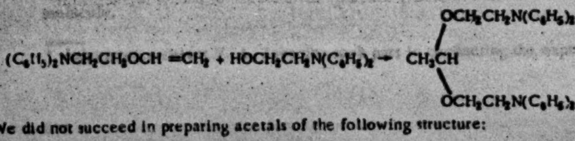
In order to weaken the effect of the basic properties of the amino group, a phenyl radical may be introduced into it. The presence of only one phenyl radical already raises the reactivity of the vinyl ether. Thus, the vinyl ether of 2-anilinoethanol $CH_2{=}CHOCH_2CH_2NHC_6H_5$ (V), unlike the ethers (I), (II), (III), and (IV), readily undergoes several reactions in presence of traces of concentrated hydrochloric acid [4]. In view of these considerations it was of interest to determine the effect of the introduction of two phenyl radicals in the amino group of the vinyl ether of 2-aminoethanol. The present paper is devoted to the synthesis of the vinyl ether of 2-diphenylaminoethanol and the investigation of its properties. The ether was prepared by the vinylation of the corresponding amino alcohol:

$$(C_6H_5)_2NCH_2CH_2OH + HC{\equiv}CH \rightarrow (C_6H_5)_2NCH_2CH_2OCH{=}CH_2 \qquad (VI)$$

Investigation of the vinylation reaction showed that reaction between 2-diphenylaminoethanol and acetylene gives a good yield of the vinyl ether (65-75%), both in presence of caustic potash and in presence of the potassium derivative of the amino alcohol, as catalyst. In a study of the chemical properties of the resulting vinyl ether it was shown that it is hydrolyzed by 2% sulfuric acid with formation of acetaldehyde and the corresponding amino alcohol. Hydolysis is slow at 20°. Heating and vigorous agitation accelerate the reaction, but when heat is applied hydrolysis is accompanied by side reactions. Hydrogenation of the vinyl ether of 2-diphenylaminoethanol over Raney nickel resulted in the synthesis of the corresponding ethyl ether:

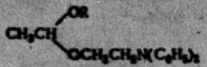
$$CH_3CH_2OCH_2CH_2N(C_6H_5)_2$$

In a study of the addition of alcohols to the vinyl ether (VI), the alcohols taken as examples were methanol, butyl alcohol, and 2-diphenylaminoethanol. It was found that, unlike other vinyl ethers of ethanolamines studies (I-V) [1, 2, 4], the ether (VI) readily formed acetals in good yield (60-65%). In this way acetaldehyde bis 2-diphenylaminoethyl) acetal was prepared:



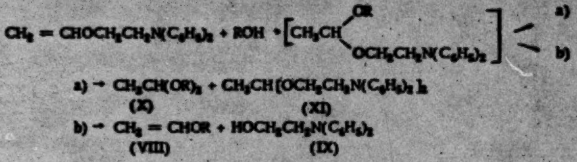
$$(C_6H_5)_2NCH_2CH_2OCH{=}CH_2 + HOCH_2CH_2N(C_6H_5)_2 \rightarrow CH_3CH\begin{cases}OCH_2CH_2N(C_6H_5)_2\\ OCH_2CH_2N(C_6H_5)_2\end{cases} \qquad (VII)$$

We did not succeed in preparing acetals of the following structure:



$$CH_3CH\begin{cases}OR\\OCH_2CH_2N(C_6H_5)_2\end{cases}$$

(R is CH_3 or C_4H_9) in a pure state, since on vacuum distillation (3 mm) they decomposed into alkyl vinyl ether (VIII) and 2-diphenylaminoethanol (IX). The presence of these two substances among the reaction products together with the isolated dialkyl acetal (X) and the bis(2-diphenylaminoethyl) acetal (XI) proves that these mixed acetals are formed. In the given case the reaction evidently proceeds as follows:



$$CH_2=CHOCH_2CH_2N(C_6H_5)_2+ROH\rightarrow\left[CH_3CH\begin{cases}OR\\OCH_2CH_2N(C_6H_5)_2\end{cases}\right]\begin{matrix}\nearrow a)\\ \searrow b)\end{matrix}$$

$$a)\rightarrow\underset{(X)}{CH_3CH(OR)_2}+\underset{(XI)}{CH_3CH[OCH_2CH_2N(C_6H_5)_2]_2}$$

$$b)\rightarrow\underset{(VIII)}{CH_2=CHOR}+\underset{(IX)}{HOCH_2CH_2N(C_6H_5)_2}$$

The polymerization of the vinyl ether of 2-diphenylaminoethanol was carried out in order to estimate its tendency to undergo this change. We succeeded in effecting polymerization both in the presence of ionic catalysts (concentrated hydrochloric acid and ferric chloride), and also in the presence of free-radical catalysts (2,2'-azobis[2-methylpropionitrile]). Under our conditions, however, the yield of polymer and the degree of polymerization were low. Products close in molecular weight to the dimer were obtained.

The behavior in the reactions of acetal formation and polymerization indicate the vinyl ether of 2-diphenylaminoethanol is more reactive not only than the vinyl ethers (I), (II), and (III), but also than the vinyl ether of 2-diethylaminoethanol (IV). Hence, the introduction of two phenyl radicals into the amino group not only excludes the effect of the hydrogen bond on the reactivity of vinyl ethers of ethanolamines, but also weakens the effect of the basic properties of the amino group to a considerable extent.

EXPERIMENTAL

I. Synthesis of the Vinyl Ether of 2-Diphenylaminoethanol*

2-Diphenylaminoethanol was prepared by reaction between diphenylamine and ethylene oxide in an autoclave at 220-240°. The yield was 60-65%. This amino alcohol is a very thick yellow liquid, which crystallizes after long standing. It has the following constants: b.p. 183-186° (5 mm); n_D^{20} 1.6210; d_4^{20} 1.121; MR 66.93; calculated for $C_{14}H_{15}ON$ MR 65.11; the literature [5] gives b.p. 169-171° (9-10 mm); d_4^{20} 1.116; n_D^{20} 1.629.

The vinylation of 2-diphenylaminoethanol was carried out in an autoclave in benzene or dioxane medium at 170-180° in presence of caustic potash or the potassium derivative of 2-diphenylaminoethanol as catalyst. The last compound was prepared by stirring and warming the amino alcohol (excess, 100-105° in flask, adding potassium (gradually, in the form of very small pieces). The results of the vinylation are given in Table 1.

Example. A mixture of 73.0 g of the amino alcohol, 8 g of its potassium derivative, and 200 ml of benzene was prepared in a two-liter autoclave, and acetylene at 14-16 atm was passed in. The amount of acetylene necessary for complete vinylation was absorbed in three hours at 180°. The reaction product was a thick dark-colored liquid, which was vacuum-fractionated. After removal of benzene, the following fractions were collected:

Fraction I, B.p. 100-158° (5 mm);	6.1 g
Fraction II, B.p. 158-165° (5 mm);	61.5 g
Resin	18.2 g

Fractions I and II were treated with sodium to remove traces of alcohol and were then distilled. The product, amounting to 61.5 g (74.5%), was the vinyl ether of 2-diphenylaminoethanol, a thick colorless liquid that rapidly yellowed in the air: b.p. 158-159° (3 mm); n_D^{20} 1.5980; d_4^{20} 1.0696; MR 76.34; Calculated for $C_{16}H_{17}ON$ MR 74.00.

The difference between the determined and calculated molecular refractions of the vinyl ether of 2-diphenylaminoethanol, and also of its derivatives, is probably to be explained by the presence of phenyl radicals in its molecule.

---

* Laboratory assistant V. A. Zabavina took part in conducting the experiments.

Found %: C 80.08; 79.90; H 7.02; 7.13; N 5.79; 5.84

$C_{16}H_{17}ON$. Calculated %: C 80.30; H 7.16 N 5.85

The literature [6] gives b.p. 150-160° (3 mm).

TABLE 1

Expt. No.	Catalyst (taken in the amount of 10% on the weight of amino alcohol)	Solvent	Duration of reaction hours	Yield of vinyl ether (%)	Amount of resin (% on weight of amino alcohol)
1	Potassium derivative	Benzene	5	75.5	28.4
2	Potassium derivative	Benzene	3	74.5	25.0
3	Potassium derivative	Dioxane	5.5	81.5	20.8
4	Caustic potash	Benzene	5	52.3	99.4
5	Caustic potash	Benzene	2.5	66.0	57.5
6	Caustic potash	Benzene	0.5	66.5	58.5

II. Hydrolysis of the Vinyl Ether of 2-Diphenylaminoethanol

The vinyl ether was hydrolyzed at 95° with 2% H_2SO_4. The hydrolysis was carried out in a three-necked flask fitted with mercury-sealed stirrer, thermometer, reflux condenser, and tube for the passage of gas. A mixture of 9.1 g of the vinyl ether and 100 ml of 2% H_2SO_4 was prepared in the flask. The acetaldehyde formed in the hydrolysis was removed by a stream of nitrogen and trapped by water in Tishchenko bottles. The acetaldehyde contents of the aqueous solutions were determined by the bisulfite method [7]. The reaction products were separated from the aqueous layer in the form of a solution in ether, and the ether solution was dried with potassium carbonate and distilled. The products were 6.6 g of 2-diphenylaminoethanol, 1.0 of acetaldehyde, and 1.3 g of a substance of molecular weight 398, which was not investigated further.

III. Hydrogenation of the Vinyl Ether of 2-Diphenylaminoethanol

The hydrogenation was carried out over Raney nickel (5% on the weight of the ether) at 100° in an autoclave. The reaction product was filtered from the catalyst, treated with sodium, and distilled. The ethyl ether of 2-diphenylaminoethanol was obtained as a colorless liquid, b.p. 158-159° (4mm); $n_D^{20.5}$ 1.5920; d_4^{20} 1.0600; MR 77.02; Calculated for $C_{16}H_{19}ON$ MR 74.47

Found %: C 79.96; 79.85; H 7.67; 7.45; N 5.91. 5.79

$C_{16}H_{19}ON$. Calculated %: C 79.63; H 7.94 N 5.80

IV. Synthesis of Acetaldehyde Bis (2-diphenylaminoethyl) Acetal (VII)

The acetal was prepared in a three-necked flask fitted with stirrer and thermometer. One drop of concentrated hydrochloric acid was added to a mixture of 8.7 g (0.036 mole) of the vinyl ether of 2-diphenylaminoethanol and 7.2 g (0.034 mole) of 2-diphenlaminoethanol (n_D^{20} 1.6220). There was a spontaneous rise of temperature, the maximum rise being 35°. Stirring was continued for four hours. The very viscous, dark-brown reaction product was vacuum-distilled, and 15.1 g of it gielded:

Fraction I, B.p.	165-280° (4 mm);	4.3 g
Fraction II, B.p.	281-288° (3.5 mm);	9.6 g
Resin		1.0 g

Redistillation of Fraction II yielded 9.5 g (62.5%) of the required acetal, a very thick, dark-yellow liquid, b.p. 282-284° (4 mm); n_D^{20} 1.6185; d_4^{20} 1.1175; MR 141.9; Calculated for $C_{30}H_{32}O_2N_2$ MR 137.5

Found %: C 79.33; 79.19; H 7.21; 7.25; N 5.95; 6.06

$C_{30}H_{32}O_2N_2$. Calculated %: C 79.61; H 7.13; N 6.19

V. Reaction of the Vinyl Ether of 2-Diphenylaminoethanol with Butyl Alcohol

The procedure described in Section IV was followed. Reaction was between 14.0 g (0.058 mole) of the vinyl ether and 4.4 g (0.059 mole) of butanol (b.p. 115-117°; n_D^{20} 1.3990). The maximum rise in temperature was 38°. Vacuum fractionation of the products yielded 2.1 of the dibutyl acetal (b.p. 184-185°; n_D^{20} 1.4110), 5.5 g of the bis (2-diphenylaminoethyl) acetal [b.p. 275-280° (2-3 mm); $n_D^{21.5}$ 1.6187 (see preceding experiment)], and 10.1 g of a product that distilled with decomposition at 175-187° (3 mm). From the decomposition products, butyl vinyl ether (b.p. 92-94°; n_D^{20} 1.4035) and 2-diphenylaminoethanol [b.p. 180-183° (4 mm); n_D^{20} 1.6210] were isolated.

VI. Reaction of the Vinyl Ether of 2-Diphenylaminoethanol with Methanol

The reaction conditions were similar to those of the synthesis of the bis (2-diphenylaminoethyl) acetal (Section IV). A mixture of 15.9 g (0.066 mole) of the vinyl ether and 4.7 g (0.145 mole) of purified methanol (b.p. 65°; n_D^{20} 1.3312) was prepared in the flask. The maximum rise of temperature after the addition of one drop of concentrated hydrochloric acid was 53°. Vacuum distillation of 18.7 g of the reaction product yielded 1.8 g of the dimethyl acetal (b.p. 63-64°; n_D^{20} 1.3762); 9.2 g of the bis (2-diphenylaminoethyl) acetal [b.p. 275-277° (2-3 mm); n_D^{21} 1.6187], and 4.9 g of a product that distilled with decomposition at 170-178° (4 mm). 2-Diphenylaminoethanol was isolated from the decomposition products ($n_D^{18.5}$ 1.6235).

VII. Polymerization of the Vinyl Ether of 2-Diphenylaminoethanol

a) Polymerization in presence of Ferric Chloride and of Concentrated Hydrochloric Acid. Ferric chloride was used as a 5% solution in butyl alcohol. The polymerization was carried out in a three-necked flask fitter with thermometer and reflux condenser. The vinyl ether 23 g was brought to the boil under reduced pressure (163-164° at 3.5-4 mm), and one drop of catalyst was added through a capillary. The ether was maintained at the boiling point for four hours. The thick dark-bordeaux product was dissolved in acetone, and the polymer was precipitated from the acetone solution with methanol. It was then washed repeatedly with methanol and dried under reduced pressure (3-5 mm). The yield and characteristics of the polymer are given in Table 2. Vacuum distillation of the acetone-methanol solution yielded the original vinyl ether and a viscous dark-colored product (22-23% yield) having a molecular weight of 448-617. Elementary analysis indicated that this substance was a polymer of the vinyl ether of 2-diphenylaminoethanol, formed as a result of the further heating during distillation.

Found %: C 79.72, 79.85; H 7.10; 7.09; N 6.17; 6.08

b) Polymerization in presence of 2,2'-Azobis [2-methylpropionitrile]. The vinyl ether (15.7 g) was heated with the catalyst (2% on the weight of the ether) in a sealed glass tube at 60° for 100 hours continuously. The treatment of the reaction product was as in the preceding experiments (Section VII, a). A thick dark-yellow polymer, molecular weight 475, was obtained in a yield of 0.4 g.

Found %: C 79.86; 79.75; H 7.28; 7.18; N 6.44; 6.42

TABLE 2

Expt. No.	Catalyst	Yield of polymer (%)	Amount of unchanged vinyl ether (%)	Molecular weight of polymer (determined cryoscopically in benzene)	Elementary analysis		
					C	H	N
1	Concentrated hydrochloric acid	31.2	38.6	420-460	80.18	7.40	5.84
					80.30	7.20	6.23
2	Ferric chloride	29.8	43.0	626	79.86	7.10	6.36
					79.97	7.11	6.40

Vacuum distillation of the acetone-methanol solution yielded 12.5 g of the original vinyl ether, 0.25 g of a sticky yellow solid (molecular weight 369), and 1.0 g of a thick resinous residue.

SUMMARY

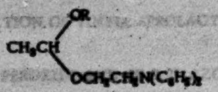
1. The vinylation of 2-diphenylaminoethanol was studied.

2. The vinyl and ethyl ethers of 2-diphenylaminoethanol were prepared and characterized.

3. It was found that the vinyl ether of 2-diphenylaminoethanol, unlike other vinyl ethers of ethanolamines, reacts with alcohols under the conditions normally required by alkyl vinyl ethers and undergoes polymerization in presence of ferric chloride and of concentrated hydrochloric acid.

4. Acetaldehyde bis (2-diphenylaminoethyl) acetal was prepared.

5. It was shown that the acetals



$$CH_3CH\begin{cases}OR\\ OCH_2CH_2N(C_6H_5)_2\end{cases}$$

in which R−CH_3 or C_4H_9, are unstable and decompose when distilled with formation of the alkyl vinyl ether and 2-diphenylaminoethanol.

LITERATURE CITED

[1] M. F. Shostakovsky and I. A. Chekulaeva, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953 No. 368 (T.p. 335)*.

[2] M. F. Shotakovsky and I. A. Chekulaeva, Bull. Acad. Sci. USSR, Div. Chem. Sci. , 1954, No. 6, 1111 (T.p. 971)*.

[3] M. F. Shostakovsky and I. A. Chekulaeva, Bull. Acad. Sci. USSR, Div. Chem. Sci. , 1955, No. 3, 544 (T.p. 481)*.

[4] M. F. Shostakovsky and I. A. Chekulaeva, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, No. 1, 146 (T.p. 127)*.

[5] S. Kanao, J. pharm. Soc. Japan 50, 50 (1930)C 1930, II, 1696.

[6] J. W. Copenhaver, M. H. Bigelow, Acetylene and Carbon Monoxide Chemistry, 1949, p. 89.

[7] M. F. Shostakovsky and E. N. Prilezhaeva, J. Gen. Chem., 17, p 1132 (1947).

Received October 20, 1954

N. D. Zelinsky Institute of Organic
Chemistry of the USSR Academy of Sciences

---

* T.p. = C. B. Translation pogination

REACTIONS OF UNSATURATED AND MACROMOLECULAR COMPOUNDS

COMMUNICATION 6. COPOLYMERIZATION OF VINYLCAPROLACTAM WITH METHYL METHACRYLATE IN PRESENCE OF BENZOYL PEROXIDE AND OF 2,2'-AZOBIS [2-METHYLPROPIONITRILE]

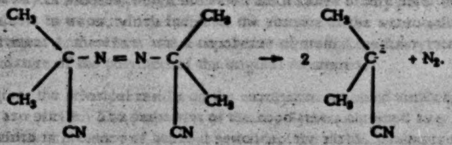
M. F. Shostakovsky, F. P. Sidelkovskaya, and A. M. Khomutov

It is known that polymers of vinylcaprolactam (2-oxo-1-vinylhexamethylenimine) are hydrophilic [1] and that polymers of methyl methacrylate are hydrophobic; it was of interest, therefore, to study the copolymerization of these monomers and to determine the effect of the nature of the monomers on the properties of the polymeric products formed.

There is very little information in the literature on the participation of vinylcaprolactam in copolymerization reactions. A patent [2] refers in a general way to the copolymerization of vinyl lactams, including vinylcaprolactam, with vinyl laurate and other vinyl esters of higher fatty acids (having not less than eight carbon atoms); the initiator used was 2,2'-azobis [2-methylpropionitrile].

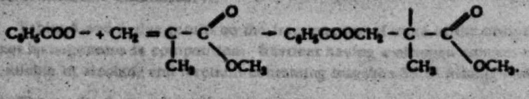
In the present investigation we studied the copolymerization of vinylcaprolactam with methyl methacrylate in presence of benzoyl peroxide and of 2,2'-azobis [2-methylpropionitrile], which initiate reactions proceeding by a free-radical mechanism. We have previously pointed out [3] that the activity of a monomer in a polymerization process varies according to the mechanism by which the reaction proceeds. It should be noted also that for a given mechanism the activity varies according to the character of the initiator. For example, initiation by benzoyl peroxide [4] and by the azo nitrile [5] results from the decomposition of these substances into radicals (Equations 1 and 2), so that in both cases the process proceeds by a free-radical mechanism:

$$(C_6H_5CO)_2O_2 \rightarrow 2C_6H_5COO- \qquad (1)$$

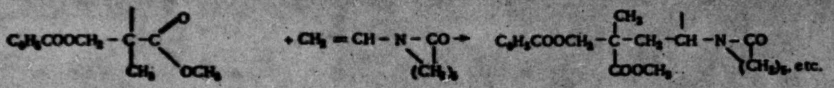


(2)

However, the effects of these initiators in activating our monomers are different: it was found that benzoyl peroxide has very little tendency to bring about the polymerization of vinylcaprolactam, but promotes vigorous polymerization in methyl methacrylate; on the other hand the azo nitrile is very active in polymerizing both of these monomers. In spite of the fact that vinylcaprolactam does not polymerize to any appreciable extent in presence of benzoyl peroxide, it readily participates in copolymerization with methyl methacrylate in presence of this initiator. We observed a similar phenomenon previously in the copolymerization of methacrylic acid and vinyl ethers [6]. In the present case the process may be represented by the following equations:

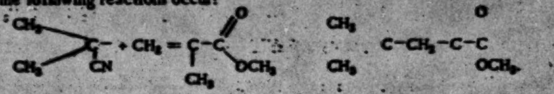


(3)

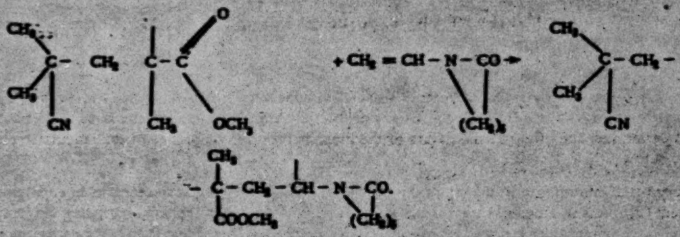


(4)

It is evident that in the copolymerization of vinylcaprolactam with methyl metacrylate in presence of the azo nitrile, the following reactions occur:



(5)



(6)

In our experiments on the copolymerization of vinylcaprolactam and methyl methacrylate, the reactants were taken in various proportions, and the results enabled us to establish the character of the process and the main laws governing its course. In Tables 1 and 2 we give the yields and compositions of the polymeric products obtained.

It will be seen from Table 1 that, when copolymerization occurs in presence of benzoyl peroxide, increase in the proportion of vinylcaprolactam in the original mixture of monomers results in a reduced yield of copolymer, but its content of vinylcaprolactam units increases. As the proportion of vinylcaprolactam increases, the viscosity of the copolymer increases a little at first, but then diminishes. The presence of nitrogen in all of the samples shows unequivocally that a copolymerization process does in fact occur, since the nitrogen-containing monomer (vinylcaprolactam) does not polymerize to any significant extent under these conditions. One of the most characteristic samples (Experiment 4, Table 1) was subjected to selective dissolution (in alcohol and water): the copolymer dissolved completely in alcohol, which indicated the absence of any pure methyl methacrylate polymer, and it was completely insoluble in water, which indicates the absence of the water-soluble polymer of vinylcaprolactam. The product of Experiment 4, therefore, was a copolymer of methyl methacrylate and vinylcaprolactam, without any appreciable admixture of the polymers of the original monomers.

Table 2 gives the principal results on the copolymerization of vinylcaprolactam and methyl methacrylate in presence of the azo nitrile. The properties of the copolymers obtained vary in the same direction as those of the copolymers obtained in presence of benzoyl peroxide; the yields, however, vary in a somewhat different way.

In order to prove that the products consisted of copolymers, and were not mixtures of two polymers, their behavior toward various solvents was studied (Table 3).

It will be seen from Table 3 that the solubility of these copolymers differs in character from the solubility of the corresponding polymers. As the proportion of vinylcaprolactam units in the copolymers increases, solubility in benzene, alcohol, and water increases. It should be noted that individual samples of similar composition do not correspond completely in their solubility relations, but the variation in such products is not unduly great. This fact must be borne in mind when inferences are made about the compositions of copolymers merely on the basis of the results of selective dissolution.

Tables 5 and 6 give results on the fractionation of some of the samples, and it will be seen that the copolymers are not homogeneous in composition: fractions having a nitrogen content of less than 5% are insoluble in water, but still soluble in alcohol; and fractions containing less than 3% of nitrogen are insoluble in alcohol.

The results that we have described indicate that a process of copolymerization occurs between vinylcaprolactam and methyl methacrylate, both in presence of benzoyl peroxide, and also in presence of 2,2'-azobis[2-methyl-

TABLE 1

Yields and Compositions of Copolymers of Vinylcaprolactam (VCL) and Methyl Methacrylate (MMA) (Catalyst: Benzoyl Peroxide)

Expt. No.	Composition of original mixture (mole-%)		Yield of copolymer (%)	η_{rel}*	N content of copolymer (%)	Proportions of monomer units (%)	
	MMA	VCL				MMA	VCL
1	100	–	94.2	–	–	100	–
1a	96	4	93.6	2.268	Traces	Not calculated →	
2	75	25	75.8	2.288	1.95	85.23	14.73
3	50	50	53.6	2.880	2.28	82.6	17.4
4	25	75	25.8	1.807	4.27	65.8	34.2
5	5	95	9.6	1.234	6.55	42.6	57.4
6	–	100	–	–	–	–	–

---

* The viscosities were measured for benzene solutions containing 1 g of polymer per 100 ml of benzene.

TABLE 2

Yields and Properties of Copolymers (Catalyst: 2,2'-Azobis [2-methylpropionitrile]

Expt. No.	Composition of original mixture (mole-%)		Yield of copolymer (%)	η_{rel}*	N content of copolymer (%)	Proportions of monomer units (%)	
	MMA	VCL				MMA	VCL
8	100	0	94.2	–	–	100	–
8a	95	5	98.0	1.771	Traces		Not calculated
9	75	25	80.1	1.970	1.95	85.7	14.3
10	50	50	77.0	2.158	4.06	67.1	32.9
11	25	75	60.0	1.536	6.69	40.75	59.25
12	5	95	76.4	1.274	7.87	27.6	72.4
14	0	100	79.6	1.172	9.72	–	100

---

* The viscosities were measured for benzene solutions containing 1 g of polymer per 100 ml of benzene.

TABLE 3

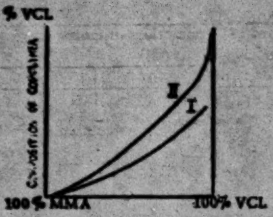
Solubilities of Copolymers of Vinylcaprolactam and Methyl Methacrylate Formed in Presence of 2,2-Azobis [2-methylpropionitrile]

Name of polymer	Composition of copolymer (mole-%)		Solvent*				
	MMA	VCL	acetone	diethyl ether	benzene	ethanol	water
Polymer of MMA	100	–	+	–	–	–	–
Copolymer 8a	Not Calculated →		+	–	⊥	T	–
Copolymer 9	85.7	14.3	+	–	⊥	T	–
Copolymer 10	67.1	32.9	+	–	+	T	T
Copolymer 11	40.75	59.25	+	–	+	T	T
Copolymer 12	27.6	72.4	+	–	+	+	T
Polymer of VCL	–	100	+	–	+	+	+

---

* + soluble; ⊥ sparingly soluble; – insoluble; T partially soluble.

propionitrile]; no evidence of the formation of the single-component polymers was obtained. In both cases the composition of the copolymer depends on the proportion of monomers in the original mixture, and the proportion of vinylcaprolactam units in the copolmer is less than in the original monomeric mixutre. This difference in composition is more marked in copolymers prepared in presence of benzoyl peroxide (see graph).



Dependence of the composition of the copolymer on that of the monomeric mixture: I) benzoyl peroxide catalyst; II) azo nitrile catalyst.

Under similar conditions, the yield of copolymer is less in the process initiated by benzoyl peroxide than in the process initiated by the azo nitrile. The results confirm that the tendency to undergo copolymerization, like the tendency of the individual monomers to undergo polymerization, depends not only on the reaction mechanism, but also on the character of the initiator used. The reaction that we have studied permits us, on the one hand, to establish a relationship between the reactivities of vinylcaprolactam and methyl methacrylate, and on the other, to synthesize new macromolecular compounds having interesting properties.

EXPERIMENTAL

The starting materials were freshly distilled and were characterized by the following constants: methyl methacrylate, b.p. 100.5°, n_D^{20} 1.4150; d_4^{20} 0.9361; vinylcaprolactam, b.p. 94-95° (4 mm) and n_D^{20} 1.5135; benzoyl peroxide was reprecipitated twice from chloroform solution by means of methanol. 2,2'-Azobis[2-methylpropionitrile] was recrystallized twice from methanol.

The polymerizations were carried out in sealed tubes in presence of 0.2% of initiator and at a temperature of 60 ± 1°. The monomers were taken in various proportions (total weight of mixture 5 g). Reaction was allowed to proceed continuously until solid or highly viscous materials were obtained (72 hours for benzoyl peroxide, 48 hours for the azo nitrile). At the end of the reaction the tubes were cooled to 0°. Control experiments on the polymerization of the monomers were carried out under the same conditions. The polymeric products were dissolved in benzene or acetone, precipitated with diethyl ether, and washed repeatedly with precipitant until tests for double bonds were negative. Precipitant was removed by decantation, and the polymers were dried to constant weight at a residual pressure of 5-6 mm and a temperature of 55-60°. They were analyzed for nitrogen content*. The solutions remaining after the precipitation of the copolymers were fractionated in order to determine the amounts of unchanged monomers.

TABLE 4

Expt. No.	Composition of original mixture (mole-%)		Weight of copolymer (g)*	Amount of vinylcaprolactam isolated (g)	Weight of undistilled residue (g)
	MMA	VCL			
1a	95	5	4.7	–	0.1
2	75	25	3.79	0.8	–
3	50	50	2.68	1.6	0.2
4	25	75	1.30	2.0	0.8
5	5	95	0.48	2.38	1.50
6	–	100	None	4.7**	–

* Original weight of monomer mixture 5 g.

** Redistillation of Sample No. 6 yielded 4.2 g of pure vinylcaprolactam and 0.4 g of resinous residue.

Copolymerization in Presence of Benzoyl Peroxide

The copolymerization was carried out by the procedure described above. The balance sheet of the reaction products is given in Table 4, and their characteristics are given in Table 1.

A sample of Copolymer No. 4 was extracted repeatedly with water, separated from the water, and dried to constant weight in a vacuum desiccator over calcium chloride. Before extraction the weight of copolymer was 0.6462 g and its nitrogen content was 4.31, 4.20%. After extraction it weighed 0.6352 g and had a nitrogen content of 4.27, 4.18%

---

* All analyses were carried out in the Microanalysis Laboratory of the Institute of Organic Chemistry of the USSR Academy of Sciences by Savvateeva, Shakurova, and Samokhotova, to whom we extend our thanks.

TABLE 5

Fractionation of Copolymers by Dissolution in Water

Sample No.	Composition of unfractionated Copolymer (mole-%)		Amount taken for fractionation (g)	N content of unfractionated copolymer (%)	Amount extracted by water		Insoluble residue	
	MMA	VCL			(g)	N content (%)	(g)	N content (%)
9	85.7	14.3	1.0741	1.95 1.94	None	–	1.010	Not determined
11	40.75	59.25	1.0676	6.69 6.76	0.4430	7.43 7.38	0.5257	4.42 4.57
12	27.6	72.4	0.5818	7.87 7.83	0.4520	7.48 7.71	0.080	4.34

TABLE 6

Fractionation of Copolymers by Dissolution in Alcohol

Sample No.	Composition of unfractionated copolymer (mole-%)		Amount taken for fractionation (g)	N content of unfractionated copolymer (%)	Amount extracted by alcohol		Insoluble residue	
	MMA	VCL			(g)	N content (%)	(g)	N content (%)
9	85.7	14.3	1.72	1.95 1.94	1.175	2.22 2.33	0.3359	1.05 1.06
10	67.1	32.9	2.15	4.06 4.03	1.759	3.97 3.83	0.2928	1.84 1.81
12	27.6	72.4	2.0	7.87 7.83	1.835	8.20 7.97	None	–

Copolymerization in Presence of 2,2-Azobis [2-methylpropionitrile]

The results of the experiments are given in Table 2. Data on the fractionation are given in Tables 5 and 6.

SUMMARY

1. A study was made of the copolymerization of vinylcaprolactam with methyl methacrylate in presence of benzoyl peroxide and of 2,2'-azobis [2-methylpropionitrile].

2. The copolymers obtained were characterized by their elementary compositions, viscosities, and solubilities.

3. It was shown that the yields and compositions of the copolymers depend on the proportion of reactants in the monomeric mixture.

4. Selective-dissolution experiments showed that the copolymers were not homogeneous in composition. No single-component polymers were detected.

LITERATURE CITED

[1] M. F. Shostakovsky, N. A. Medzykhovskaya, and M. G. Zelenskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, No. 4, 682 (T.p. 627)*, M. F. Shostakovsky, F. P. Sidelkovskaya, and M. G. Zelenskaya, Bull Acad. Sci. USSR, Div. Chem. Sci., 1952, No. 4, 690 (T.p. 633)*.

[2] J. H. Werntz, U. S. Patent 2,497705 (1950); C. 1951, I, 401.

[3] M. F. Shostakovsky and coworkers, in the Collection "Macromolecular Compounds", No. 12, 56 (1952).

[4] M. F. Shostakovsky, E. P. Gracheva, and V. A. Neterman, J. Gen. Chem., 23, 55 (1953).(T.p. 51)*

[5] C. G. Overberger, M. T. O'Shaughnessy, H. Shalit, J. Am. Chem. Soc. 71, 2661 (1949).

[6] M. F. Shostakovsky and A. M Khomutov, Bull. Acad. Sci. USSR Div. Chem. Sci., 1953, No. 6, 1048 (T.p. 931)*.

Received October 20, 1954

N. D. Zelinsky Institute of Organic Chemistry of the USSR Academy of Sciences

---

* T.p. = C. B. Translation pagination

MACROMOLECULAR COMPOUNDS

COMMUNICATION 79. PRODUCTS OF THE POLYCONDENSATION OF DIALDEHYDES AND DIKETONES WITH DIAMINES AND GLYCOLS

V. V. Korshak and S. V. Vinogradova

Dialdehydes, diketones, and keto acids all have very reactive carbonyl groups, which readily react with amines, alcohols, and other compounds containing mobile hydrogen atoms. The ability of carbonyl compounds, such as aldehydes, to undergo these reactions has found practical application for a long time in the preparation of synthetic resins, for example, the three-dimensional condensation products of formaldehyde with phenols, aniline, urea, and other substances. An extensive literature is devoted to the study of these reactions [1]. However, the use of carbonyl compounds for the preparation of linear polymers has remained almost without investigation, except in a few studies, which we shall now discuss briefly. With the object of preparing linear polymers Korshak and Pozhiltsova [2] investigated the reaction of (4,4'-biphenylene) dihydrazine with 2,4-pentanedione, 2,3-butanedione, and terephthalaldehyde and obtained the first members of the class of polyhydrazones; at the same time they showed that the molecular weight of the polyhydrazone is reduced by the presence of excess of one of the reactants. Erlenmeyer and Büchler [3] obtained linear polymers containing thiazole nuclei by the polycondensation of the dithio amides of adipic, azelaic, and oxalic acids with dihalo diketones, such as 1,4-dibromo-2,3-butanedione, 1,8-dichloro-2,7-octanedione, and 1,11-dichloro-2,10-undecanedione. Krässig and Greber [4] prepared condensation products of terephthalaldehyde with various diamines of the type $NH_2(CH_2)_n-X-(CH_2)_nNH_2$, in which X = O or NH, which they considered to be cyclic substances having rings of 26-30 atoms, without giving any proof in support of their view. Franke and Gigerl [5], and later Carothers [6], showed that aldehydes react with glycols with formation of polyacetals.

EXPERIMENTAL

The object of the present investigation was to bring about reaction between various bifunctional carbonyl compounds with diamines and glycols in order to determine whether linear polymers could be prepared. For this purpose reactions were carried out between 1,6-hexanediamine and carbonyl compounds, such as 2,3-butanedione, 2,4-pentanedione, pyruvic acid, and terephthalaldehyde, and also the reaction of the last compound with ethylene glycol and with 1,6-hexanediol. The products obtained were characterized.

In the reactions between 1,6-hexanediamine and carbonyl compounds, the reactants were taken in a molar ratio of 1 : 1; the reactions were carried out in an atmosphere of nitrogen, and heat was applied. Heat was not applied until the reactants had been mixed together, and reaction sometimes began in the cold with evolution of heat so that a certain amount of cooling had to be applied at first. The temperature of the mixture was raised gradually to 180° in the case of terephthalaldehyde, and to 110° in all other cases. The duration of the heating was 11-20 hours. The stream of nitrogen was then turned off and the mixture was heated further for 8-15 hours at a residual pressure of 1-2 mm. The properties of the products are given in Table 1.

The reactions between 1,6-hexanediamine and the carbonyl compounds listed in Table 1 result in the formation of polymers, which may be either solid or liquid, depending on the nature of the original reactants. When we arrange the original reactants in order of the melting points of the polymers that they form, we obtain the following series: 2,4-pentanedione, pyruvic acid, 2,3-butanedione.

These changes in melting point can be correlated with changes in solubility. The condensation product from 2,4-pentanedione is considerably more soluble in an alcohol-chloroform mixture than the products formed by 2,3-butanedione and by pyruvic acid. Here we can clearly see the effect of the methylene group separating the two carbonyls in 2,4-pentanedione in lowering the melting point and raising the solubility.

When the condensation product from 1,6-hexanediamine and terephthalaldehyde is not given the vacuum treatment it is still soluble in cresol, but after being heated in a vacuum it becomes insoluble in all organic solvents, though it is dissolved by dilute hydrochloric acid, which evidently brings about its degradation.

TABLE 1

Second component	Properties of reaction product				Appearance and solubility
	M.p. (°C)	Elementary analysis (%)			
		C	H	N	
Terephthalaldehyde	188-192	76.50 76.58	8.49 8.65	10.23 10.12	Clear reddish solid. Insoluble in organic solvents
2,3-Butanedione	Does not melt	72.31 72.12	10.11 10.16	13.68 13.44	Dark-colored solid, soluble in an alcohol-chloroform mixture
2,4-Pentanedione	Vaseline-like	67.69 67.70	10.59 10.56	14.31 14.43	Viscous reddish mass
Pyruvic acid	76-85	59.22 59.43	9.40 9.53	12.73 12.76	Dark-colored solid, soluble in an alcohol-chloroform mixture

TABLE 2

Empirical formula	Degree of polymerization	Content (%)		
		C	H	N
$C_{22}H_{26}O_2N_2$	1	75.43	7.43	8.00
$C_{36}H_{46}O_2N_4$	2	76.49	8.07	9.82
$C_{50}H_{66}O_2N_6$	3	76.73	8.44	10.74
Found	–	76.50	8.49	10.23
	–	76.58	8.65	10.12

No special experiments were made to determine the structures of the products that we had obtained, but the results of elementary analysis lead us to suppose that they were formed as a result of reaction between the amino groups of the 1,6-hexanediamine and the carbonyl groups of the second component. It is known that the first stage of the reaction of an aldehyde or ketone with an amine or amide is the formation of a hydroxyl-containing condensation product in accordance with the scheme:

$$RCH = O + H_2NR' \rightarrow RCH(OH)\,NHR'.$$

When heated, and sometimes in the cold, this product loses water with formation of an unsaturated compound in accordance with the scheme:

$$RCH\,(OH)\,NHR' \rightarrow H_2O + RCHNR'.$$

Carbon, hydrogen, and nitrogen determinations on our products showed that they were substances of the second type, formed by elimination of water. The products were of low molecular weight. For example, the condensation product from terephthalaldehyde and 1,6-hexanediamine was found to have a molecular weight lying between 600 and 800, its probable structure being as follows:

$$O = HCC_6H_4CH = [\,= NH\,(CH_2)_6NH = CHC_6H_4CH = \,]_x = O\text{*}$$

in which x lies between 2 and 3. It is most probable that the product was a mixture of molecules having degrees of

---

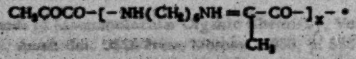
* This formula and the empirical formulas and calculated C, H, and N contents given in Table 2 are here presented exactly as in the original. It will be clear, however, that the hydrogens attached to the nitrogens should be omitted from the formula, and the formulas and figures in Table 2 need to be corrected accordingly. The entries in Table 2 should read $C_{22}H_{24}O_2N_2$, 75.86% C, 6.90% H, 8.05% N; $C_{36}H_{42}O_2N_4$, 76.87 % C, 7.47% H, 9.97% N; $C_{50}H_{60}O_2N_6$, 77.32% C, 7.73% H, 10.82% N; as in the original, calculations are based on integral atomic weights. There is a similar error in the formula for the pyruvic acid condensation product, in which the hydrogen on the second nitrogen should be omitted. With this correction the empirical formula for x = 2 is $C_{21}H_{36}O_5N_4$, for which the analysis should be (%): C 59.43; H 8.49; N 13.21. — Publisher.

polymerization of 2 and 3. Table 2 gives carbon, hydrogen, and nitrogen contents calculated for different values of the degree of polymerization.

Owing to its high volatility, 1,6-hexanediamine was lost in the course of the reaction to a greater extent than the aldehyde: this explains the fact that the terminal groups were aldehyde residues.

In view of the structure that we have proposed for the condensation products, we must give some consideration to the work of Krässig and Greber [4], who assigned a cyclic structure (30-membered ring) to substances formed by the condensation of terephthalaldehyde with 3,3-oxybispropylamine. The impossibility of the formation of such rings as the result of a condensation process is quite obvious from stereochemical considerations, and these authors gave no experimental proof of their proposed structure in their paper.

The structure of the condensation product from 1,6-hexanediamine and pyruvic acid may be represented by an analogous formula:



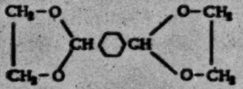
$$CH_3COCO-[-NH(CH_2)_6NH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CO-]_x-{}^{*}$$

in which $x = 2$, as can be readily seen by comparison of the analytical figures for the product with the calculated figures for the above formula:

Found %: C 59.22; 59.43; H 9.40; 9.53; N 12.73; 12.76
$C_{21}H_{38}O_5N_4$. Calculated %: C 59.15 H 8.92; N 13.14

In the reactions with 2,3-butanedione and 2,4-pentanedione, products were obtained having nitrogen contents that differed appreciably from the calculated values, which must be associated with the high volatility of the reactants and their tendency to undergo oxidation, particularly during the long period of heating. There can be no doubt, however, that here also the products were of low molecular weight and had similar structures.

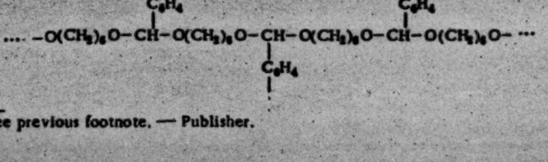
A different result was obtained in the reactions of terephthalaldehyde with glycols. In the reaction with ethylene glycol no macromolecular products were formed, but a cyclic diacetal of terephthaladehyde and ethylene glycol was obtained:



This diacetal is a white crystalline substance melting at 79-80°.

In this case, as in others in which a five- or six-membered ring can be formed, cyclization predominates over linear-polymer formation, so that a cyclic product is obtained – in this case the diacetal of terephthalaldehyde. The reaction of terephthalaldehyde with 1,6-hexanediol resulted in the formation of a three-dimensional polyacetal. The product was an elastic rubberlike mass, insoluble in organic solvents. Its dissolution could be effected only with cresol, which evidently degraded the three-dimensional polymer, since the solutions obtained were of low viscosity.

The formation of a three-dimensional polymer becomes quite understandable when it is remembered that the reaction of glycols with monoaldehydes results in the formation of linear polyacetals, which was shown by Franke and Gigerl [5], and also by Carothers [6]. As terephthalaldehyde contains two aldehyde groups, its reaction with 1,6-hexanediol leads to the formation of a three-dimensional network in which phenylene groups act as bridges linking individual polyacetal chains together, as indicated in the following scheme:



*** See previous footnote. — Publisher.**

We attempted to modify the polyacetal in order to increase its solubility: we added octyl alcohol to the reaction mixture and then heated it. However, the attempt was not successful: the product was insoluble, and was similar to that obtained in absence of the monohydric alcohol.

SUMMARY

1. It was shown that, in the reactions of 1,6-hexanediamine with terephthalaldehyde, with 2,3-butanedione, with 2,4-pentanedione, and with pyruvic acid, condensation products of similar structure are formed.

2. It was found that reaction of terephthalaldehyde with ethylene glycol results in the formation of a cyclic diacetal, whereas its reaction with 1,6-hexanediol gives a three-dimensional polyacetal.

LITERATURE CITED

[1] V. V. Korshak, Methods of Macromolecular Organic Chemistry, Vol. 1, General Methods for the Synthesis of Macromolecular Compounds, Acad. Sci. USSR Press, Moscow, 1953, p. 536 et seq.

[2] V. V. Korshak and E. A. Pozhiltsova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1950, 412.

[3] H. Erlenmeyer, W. Büchler, Helv. chim. Acta,29, 1924 (1946).

[4] H. Krässig, G. Greber, Macromol. Chem., 11, 231 (1953).

[5] A. Franke, E. Gigerl, Monatsh.,49, 8 (1928).

[6] W. H. Carothers, Chem. Rev.,8, 353 (1931).

Received April 14, 1954

Institute of Heteroorganic Compounds
of the USSR Academy of Sciences

MACROMOLECULAR COMPOUNDS

COMMUNICATION 80. A CASE OF MIGRATIONAL COPOLYMERIZATION

V. V. Korshak and S. V. Vinogradova

Migrational polymerization is a polymerization process characterized by the occurrence of hydrogen transfer in each elementary act of the reaction [1]. Polymerization reactions of this type, which has received very little study, include the copolymerization of diisocyanates and glycols [1] and the copolymerization of diolefins, such as 1,5-hexadiene, 2,6-diallylphenyl acetate, 1,6-heptadien-4-ol, and 1,5-diphenyl-3-pentadienone with various dithiols [2].

An interesting reaction in this connection is that of the addition of alcohols and amines to the double bond in various acrylic and methacrylic derivatives. It is known that acrylonitrile [3], acrylic acid [4], and methacrylic esters [5] readily combine at the double carbon-carbon bond with alcohols, thiols, amines, and other compounds having mobile hydrogen atoms and form addition products (derivatives of 3-substituted propionic acid):

$$ROH + CH_2 = CHCOOR' \rightarrow RO-CH_2CH_2COOR'.$$

In this paper we give the results of preliminary experiments in which it was shown that polymers may be obtained by the addition of glycols, diamines, and amino alcohols to diacrylic or dimethacrylic esters of glycols.

EXPERIMENTAL

The unsaturated compounds used were ethylene diacrylate, ethylene dimethacrylate, and hexamethylene dimethacrylate, which were prepared by heating a mixture of the appropriate acid and glycol in presence of sulfuric acid, benzene, and an inhibitor (hydroquinone). Addition reactions were carried out between these acrylic and methacrylic esters and 1,6-hexanediamine, ethylene glycol, and 1,3-diamino-2-propanol.

Experimental Procedure

Mixtures of reactants were prepared in glass tubes, which were freed from air by repeated sequences of evacuation and filling with pure nitrogen, and then sealed. The sealed tubes were then placed in a thermostat, which maintained the temperature within the required range. An inhibitor was present in each tube, hydroquinone and dinitrobenzene being used for this purpose. Inhibitors were used in order to avoid the occurrence of radical polymerization. A control experiment was included in each series, the tube then containing only the diacrylic or dimethacrylic ester and inhibitor. No polymerization occurred in the control experiments, so that the formation of polymer in the other tubes was to be attributed to migrational, not radical polymerization.

Copolymerization with 1,6-Hexanediamine

The experiments on the copolymerization of 1,6-hexanediamine with ethylene dimethacrylate, with ethylene diacrylate, and with hexamethylene dimethacrylate were carried out at 50°, 110°, and 150° at molar ratios of ester to diamine of 1 : 1 and 1 : 0.5 and for various periods of time (from a few hours to 80 hours).

The products obtained at 50° with a heating period of up to 80 hours were clear colorless plastic substances, readily soluble in acetic acid and in an alcohol-chloroform mixture. The products obtained at 110° were soluble only when heating was for not more than nine hours. Further heating resulted in the formation of clear colorless substances that were not soluble. The products obtained at 150° were soluble only when heating was for not more than three hours, more prolonged heating resulting in the formation of insoluble substances. Reaction with ethylene diacrylate was more rapid than with ethylene dimethacrylate.

The product obtained by reaction of 1,6-hexanediamine with an equimolecular amount of ethylene dimethacrylate at 150° for 17 hours was washed with alcohol, water, and ether, and then dried. A powder was obtained which was insoluble in organic solvents; its elementary composition was (%): C 60.42; 60.38; H 9.68; 9.74; N 9.40; 9.41

The linear reaction product in the copolymerization of 1,6-hexanediamine with ethylene dimethacrylate in accordance with the equation:

$$xCH_2=C(CH_3)COO(CH_2)_2OOCC(CH_3)=CH_2+xH_2N(CH_2)_6NH_2\rightarrow$$
$$\rightarrow[-CH_2-CH(CH_3)COO(CH_2)_2OOCCH(CH_3)CH_2-NH(CH_2)_6NH-]_x.$$

would have the composition (%): C 61.11; H 9.55; N 8.91. The somewhat higher carbon content suggests that the analyzed product was a three-dimensional polymer and had extra ethylene dimethacrylate units incorporated in its structure.

The formation of soluble polymers in the first stages of the reaction and their conversion into three-dimensional polymers during further heating indicate that at first only one hydrogen of the amino group reacts, but at a later stage the second hydrogen also reacts.

Copolymerization with Ethylene Glycol

The experiments on the copolymerization of ethylene glycol with ethylene dimethacrylate and with ethylene diacrylate were carried out at 50° and at 110° in presence of the sodium derivative of the glycol (2.5% or 5% on the weight of ethylene glycol) as catalyst. Reaction times of up to 140 hours were used.

The reaction products were clear liquids, readily soluble in acetic acid and in an alcohol-chloroform mixture. The reaction product obtained by heating ethylene dimethacrylate with an equimolecular amount of ethylene glycol for 100 hours in presence of 2.5% of the sodium derivative of the glycol was treated with water to remove catalyst, washed with ether, carefully dried, and analyzed with the following results (%): C 55.48; 55.70; H 7.02; 6.97.

The polymer would be expected to have the following structure:

$$(-OCH_2CH_2OCH_2CH(CH_3)COOCH_2CH_2OOCCH(CH_3)CH_2-)_x.$$

Its analysis should be (%): C 55.37; H 7.69. It will be seen by a comparison of the determined and calculated carbon and hydrogen contents that the polymer obtained was a copolymer of ethylene glycol and ethylene dimethacrylate of the structure given above.

One of the products obtained by reaction between ethylene diacrylate and ethylene glycol was purified in a similar way and analyzed with the following results (%): C 51.68; 51.63; H 6.66; 6.45. For the expected polymer $(-OCH_2CH_2OCH_2CH_2COOCH_2CH_2OOCCH_2CH_2-)_x$ the analysis should be (%): C 51.72; H 6.89. For the copolymer of ethylene glycol with ethylene diacrylate the determined and calculated carbon and hydrogen contents are in sufficiently close agreement.

Copolymerization with 1,3-Diamino-2-propanol

Experiments on the copolymerization of 1,3-diamino-2-propanol with ethylene dimethacrylate and with ethylene diacrylate were carried out at various molar ratios (from 1 : 1 to 2 : 5) at 110° for 30 hours (of which 13 hours were under vacuum conditions). In some experiments an additional 2.5% of the sodium derivative of 1,3-diamino-2-propanol was made, as catalyst. In all cases transparent, slightly greenish or yellowish, somewhat elastic solids, insoluble in organic solvents, were obtained as products. The hardest products were obtained when the molar ratio of reactants was 1 : 1.

DISCUSSION OF RESULTS

It may be inferred from the results that the acrylic and methacrylic esters of ethylene glycol and 1,6-hexanediol are able to undergo copolymerization with diamines, glycols, and amino alcohols. The reaction leads to the formation of linear and three-dimensional compounds, which are polyesters in which ether or imino linkages alternate with ester groupings. Polymers of this type were previously unknown; they may be prepared also by the polycondensation of ethylene glycol or 1,6-hexanediol with dicarboxylic acids containing ether or imino linkages in their chains.

The copolymerization of acrylic and methacrylic esters with glycols belongs to a type of polymerization processes that closely resemble the copolymerization reactions between glycols and diisocyanates. Reactions of this type are characterized by the occurrence of hydrogen transfer in each elementary act of the reaction. It is therefore desirable to refer to this type of reactions as "migrational copolymerization", as suggested by one of us and Gribova [6].

SUMMARY

1. The reactions of 1,6-hexanediamine with ethylene dimethacrylate, with hexamethylene dimethacrylate, and with ethylene diacrylate were investigated. [illegible]

2. The reactions of ethylene diacrylate and of ethylene dimethacrylate with ethylene glycol and with 1,3-diamino-2-propanol were investigated.

3. It was found that, in the reaction of the acrylic and methacrylic esters of glycols with glycols, diamines, and amino alcohols, copolymers are formed by the mechanism of migrational copolymerization.

LITERATURE CITED

[1] V. V. Korshak, Methods of Macromolecular Organic Chemistry, Volume 1. General Methods for the Synthesis of Macromolecular Compounds, Acad. Sci. USSR Press, Moscow, 1953, pp. 9, 323.

[2] V. V. Korshak and I. A. Gribova, Proc. Acad. Sci. USSR, 82, 397 (1952).

[3] H. A. Bruson, T. W. Riener, J. Am. Chem. Soc., 65, 23 (1943).

[4] T. Prudie, W. Marschall, Soc., 59, 474.

[5] C. A. Weisel, R. B. Taylor, H. S. Mosker, F. C. Whitmor, J. Am. Chem. Soc., 67, 1071 (1945).

[6] V. V. Korshak and I. A. Gribova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 3, 550 (T.p. 467)*.

---

* T.p. = C. B. Translation pagination

MACROMOLECULAR COMPOUNDS

COMMUNICATION 81. MIXED POLYAMIDES CONTAINING GLUTARIC OR PIMELIC ACID RESIDUES

V. V. Korshak and T. M. Frunze

We have previously described mixed polyamides prepared by the polycondensation of 1,6-hexanediamine with mixtures of various proportions of two dicarboxylic acids [1]. The mixed polyamides investigated contained residues of succinic, adipic, suberic, azelaic, and sebacic acids, which, apart from azelaic acid, contain even numbers of carbon atoms in their molecules. The results obtained, therefore, did not give a sufficiently clear picture of the effect of the evenness or oddness of the number of carbon atoms in the dicarboxylic acid on the properties of the polyamides obtained.

With the object of making a more detailed investigation of the effect of the presence of a dicarboxylic acid residue having an odd number of carbon atoms on the properties of mixed polyamides, we have prepared mixed polyamides containing glutaric or pimelic acid residues together with residues of dicarboxylic acids such as adipic, azelaic, and sebacic, present in various proportions.

In the polycondensation experiments and in the investigation of the products, the procedure was the same as that used in previous investigations [1, 2]. The dicarboxylic acids used had the following constants: glutaric acid, m.p. 97-98° (the literature [3] gives 97° and 98°), and pimelic acid, m.p. 104-105° (the literature [4] gives 105-105.5). The 1,6-hexanediamine salts of glutaric and pimelic acids were prepared by the method described previously [1] and had the following constants: 1,6-hexanediamine glutarate, m.p. 150°, and 1,6-hexanediamine pimelate, m.p. 161-162°. The other dicarboxylic acids and their 1,6-hexanediamine salts had the constants given previously [1].

DISCUSSION OF RESULTS

The mixed polyamides that we prepared were white opaque horny substances. They could be readily spun from the melt into fibers capable of being cold-drawn. They were very sparingly soluble in ethanol. The dependence of the melting points of the polyamides on their compositions is shown in Table 1.

Table 1 shows that polyamides in which one original component is glutaric or pimelic acid have melting points that vary with composition: the curves for this variation have minima as in the systems investigated previously [1, 2]. This dependence of melting point on the original proportions of reactants is shown graphically in Figures 1 and 2.

The products having the lowest melting points contain a mole fraction of 0.6 of the "odd" acid residue. The low melting points of polyamides derived from odd dicarboxylic acids are to be explained by the fact that not all of the amide groupings in the macromolecular chain are able to interact with amide groupings of neighboring chains with formation of hydrogen bonds. This fact, first noted by Hill and Walker [5], was considered in detail by us in the preceding communication, and in the same paper we demonstrated the effects of even and odd numbers of carbon atoms in the dicarboxylic acid molecule and the effects also of such factors as the chain length of the dicarboxylic acid, diamine, or amino acid.

It was found that with increase in the chain length of the dicarboxylic acid, diamine, or amino acid, the extent of hydrogen bonding between amide groupings of different macromolecules increased. Thus it therefore follows that in in 5,7-nylon $[-NH(CH_2)_5NH-CO(CH_2)_5CO-]_x$ only 50.21% of the amide groupings were found to be capable of forming hydrogen bonds with neighboring macromolecules, whereas in 5,13-nylon $[-NH(CH_2)_5NH-CO(CH_2)_{11}CO-]_x$ the number of hydrogen-bonded amide groupings had risen to 75.32% [6]. Hence, lengthening of the molecules of the reactants, i.e. of the repeating unit of the macromolecule, results in the facilitation of the formation of hydrogen bonds between amide groupings. It may be expected, therefore, that, when the repeating unit is sufficiently long, even polyamides derived from an odd diamine and an odd dicarboxylic acid will be able to form fully hydrogen-bonded systems in which all the amide groupings take part in hydrogen bonding. There will then be complete agreement between the melting points calculated from our proposed formula [7]:

$$y = 7x + 110,$$

(y is the melting point of the polyamide; x is the percentage of the amide groupings that are hydrogen-bonded) and the experimentally observed melting points of the polyamides.

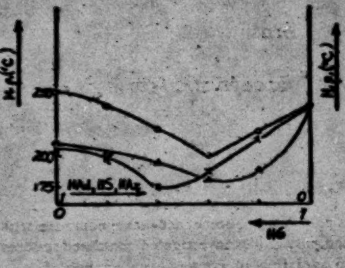


Figure 1

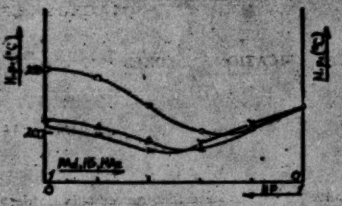


Figure 2

TABLE 1

Melting Points of Mixed Polyamides (°C)

Molar ratio of reactants **	Names of reactants					
	HAd* / HG	HAz / HG	HS / HG	HAd / HP	HAz / HP	HS / HP
1.0/0.0	250-252	205-208	210-212	250-252	205-208	210-212
0.8/0.2	240-241	199-200	202-205	244-246	197-199	205-208
0.6/0.4	220-222	176-178	195-197	221-222	186-188	193-195
0.4/0.6	200-202	186-189	180-183	200-202	191-192	188-189
0.2/0.8	220-221	214-215	185-187	204-206	205-209	203-205
0.0/1.0	240-241	240-241	240-241	220-225	220-225	220-225

* Abbreviations: Ad adipic acid; Az azelaic acid; S sebacic acid; G glutaric acid; P pimelic acid; H 1,6-hexanediamine.

** The numerator and denominator refer, respectively, to the salts indicated in the numerator and denominator under the heading "Names of reactants".

Examination of Figures 1 and 2 shows that in systems derived from adipic acid (HAd–HG and HAd–HP) the minimum melting points are the same, although, in view of the difference in the chain lengths of glutaric and pimelic acids, a difference would be expected. Comparison of the melting points of the systems HAz–HG and HAz–HP and also of HS–HG and HS–HP shows that in these cases the lower minimum temperatures are found in the systems containing glutaric acid residues, not pimelic acid residues, although analogy with previous results would lead one to expect the opposite.

It is probable that these discrepancies in the values of the melting points are to be explained on the basis of the considerations already given in which the melting point is associated with the possibility of the formation of a larger or smaller number of hydrogen bonds, which in its turn depends on the length of the repeating unit of the macromolecule. As pimelic acid has a longer chain than glutaric acid, the opportunities for hydrogen bonding between amide groupings will be greater in the polyamides containing the longer pimelic acid. Hence, up to a certain limit, the melting points of polyamides containing a certain proportion of glutaric acid residues will be lower than those of polyamides derived from pimelic acid.

In the glutaric acid systems investigated the highest minimum m.p. was found in the system HAd-Hg, the lowest in the system HAz-HG, and the minimum m.p. of the system HS-HG is intermediate. The pimelic systems present a similar picture; the system HAd–HP has the highest and the system HAz–HP the lowest minimum melting points, and the system HS–HP is intermediate. Hence, in all cases, the lowest minimum melting point is found in systems derived from two dicarboxylic acids having odd numbers of carbon atoms or methylene groups in their molecules.

TABLE 2

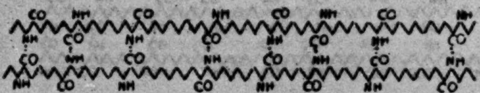
Variation in the Number of Amide Groupings and Number of Hydrogen Bonds (per 100 Methylene Groups) with Variation in the Composition of Mixed Polyamides

Names of reactants *	Molar ratio of reactants	Melting point of polyamide (°C)	Number of amide groupings per 100 methylene groups	Melting point calculated from proportion of amide groupings (°C)	Number of hydrogen-bonded amide groupings per 100 methylene groups	Percent of the amide groupings that are hydrogen-bonded
HAd/HS	1.0/0.0	250	20.00	250	20.00	100.0
"	0.8/0.2	220	18.52	240	15.72	84.83
"	0.6/0.4	190	17.24	230	11.43	66.29
"	0.5/0.5	190	16.66	226	11.43	68.60
"	0.4/0.6	185	16.13	223	10.71	66.39
"	0.2/0.8	190	15.15	216	11.43	75.44
"	0.0/1.0	210	14.28	210	14.28	100.0
HAd/HP	1.0/0.0	250	20.00	250	20.00	100.0
"	0.8/0.2	244	19.60	247	19.14	97.65
"	0.6/0.4	221	19.23	245	15.85	82.46
"	0.4/0.6	200	18.86	242	12.85	68.13
"	0.2/0.8	204	18.51	239	13.43	72.55
"	0.0/1.0	220	18.18	237	15.71	86.41
HAz/HP	1.0/0.0	205	15.33	217	13.58	88.23
"	0.8/0.2	197	15.87	221	12.43	78.32
"	0.6/0.4	186	16.39	225	10.85	66.19
"	0.4/0.6	191	16.94	228	11.57	68.23
"	0.2/0.8	205	17.54	233	13.57	77.36
"	0.0/1.0	220	18.18	237	15.71	86.41

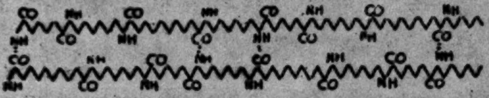
- The abbreviations are the same as in Table 1.

The question of the causes of the low melting points of mixed polyamides as compared with the melting points of single-component polyamides prepared from the same original substances, was considered by us previously [1, 2]. The proposed explanation was based on the assumption of an irregular distribution of units of different structure along the length of the macromolecular chain – this assumption being based on analogy with copolymers of the vinyl type. The possibility of the irregular distribution of units of different structure along the length of the macromolecular chain is quite a feasible one. Thus, we have shown that mixed polyamides of identical composition may have melting points that differ according to the duration of heating, i.e. according to the completeness with which polycondensational equilibrium is attained [8]. At the same time, the fact that we can obtain mixed polyamides of identical composition and identical melting point in different experiments shows that it is quite possible to attain identical states representing fairly complete polycondensational equilibrium. The regularity of the distribution of the units will then be at its maximum. It is then necessary to seek the cause of the presence of a minimum on the melting point curve in the difference of the arrangement of the macromolecular chains. In order to examine this matter we calculated the numbers of amide groupings and hydrogen bonds (per 100 methylene groups) in polyamides of various compositions (Table 2).

For simplicity we shall first examine the case of the system HAd–HS at a molar ratio of 1 : 1. When complete equilibrium is attained, it is to be expected that there will be a regular distribution of the different kinds of units along the length of the chain, as shown in the following scheme:



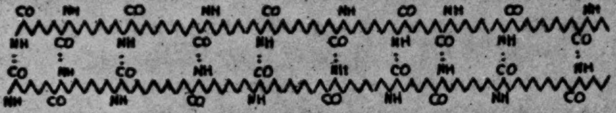
When the mutual disposition of the units of different macromolecules is such that identical units fall together, all amide groupings are able to form hydrogen bonds of the highest stability (dotted lines). Hence, with such a distribution of units it is impossible for the melting point to be lowered and for a minimum to be formed on the melting point curve. However, for a mixed polyamide of this composition another distribution of units of the macromolecules is possible and is shown in the following scheme:


CO NH CO NH CO NH CO NH
NH CO NH CO NH CO NH CO
CO NH CO NH CO NH CO NH
NH CO NH CO NH CO NH CO

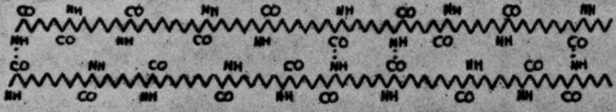
In this case only one-half of the amide groupings can form hydrogen bonds with neighboring macromolecules. If it is assumed that the two arrangements of macromolecules are equally probable, then we can estimate that roughly 75% of the amide groupings are hydrogen-bonded. According to our calculations (Table 2), the actual proportion is 68.60%. When it is considered that our calculations do not take a large number of steric factors into account, the agreement can be regarded as satisfactory.

These considerations retain their significance whatever may be the proportions of the reactants, but in addition we then have the effect of the irregular structure of the macromolecule along the length of its chain. The effect of this factor was considered by us in previous papers [1, 2]. We shall consider here the affect of a combination of the two factors.

In the system HAd–HS, molar ratio 2 : 3, the units of the macromolecular chain are distributed less regularly, as shown in the following scheme:

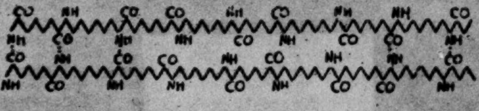

CO NH CO NH CO NH CO NH CO NH
NH CO NH CO NH CO NH CO NH CO
CO NH CO NH CO NH CO NH CO NH
NH CO NH CO NH CO NH CO NH CO

Here again, however, it is possible to arrange the macromolecules so that all of the amide groupings are hydrogen-bonded, in the manner shown. But for any other relative disposition of the macromolecules the extent of hydrogen bonding is reduced greatly, as shown in the following scheme:

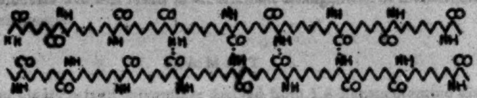

CO NH CO NH CO NH CO NH CO NH
NH CO NH CO NH CO NH CO NH CO
CO NH CO NH CO NH CO NH CO NH
NH CO NH CO NH CO NH CO NH CO

It now becomes clear why polyamides prepared from the reactants in the molar ratio of 2 : 3 have much fewer opportunities of hydrogen bonding. The data in Table 2 show that the proportion of the amide groupings that are hydrogen-bonded is practically the same for the molar ratio 2 : 3 as for the ratio 3 : 2, but the absolute numbers of hydrogen bonds (per 100 methylene groups) are different. The absolute number is less when the longer acid is in excess – in this case sebacic acid – and this explains the occurrence of a minimum on the melting point curve and the position of this minimum.

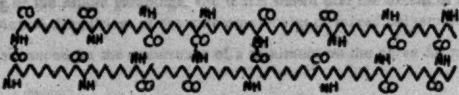
For mixed polyamides derived from odd dicarboxylic acids the picture is still more complicated. Thus, in the system HAd–HP, molar ratio 1 : 1, we may have the following arrangement:


CO NH CO CO NH CO NH NH CO
NH CO NH NH CO NH CO CO NH
CO NH CO CO NH CO NH NH CO
NH CO NH NH CO NH CO CO NH

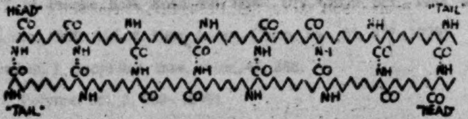
In this case there is no possible disposition of the macromolecules in which all the amide groupings can be hydrogen bonded; thus we have the following arrangement:



In systems derived from two dicarboxylic acids containing odd numbers of carbon atoms – or, what amounts to the same, methylene groups – the mutual dispositions of the macromolecules can be represented (the example taken being the system HAz–HP, molar ratio 1 : 1) as follows:

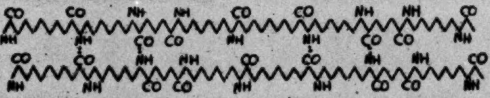


This system, like polycaprolactam, has vector macromolecules, i.e. macromolecules in which the structure reads differently according as we regard the molecule in the direction from left to right or in the reverse direction. It is here possible to form hydrogen bonds with all of the amide groupings when the chains are arranged so that they lie alternately in head-to-tail and tail-to-head directions, as follows:



However, in such a combination only half of the total number of amide groupings are utilized, the other half being disposed in such a way that, as in the preceding scheme, they may form hydrogen bonds only with part of the amide groupings of neighboring macromolecules. Hence, the occurrence of such a disposition of macromolecules that it becomes possible to form an increased number of hydrogen bonds, as indicated in the above scheme, results merely in an increase in the total number of hydrogen bonds in such a mixed polyamide to a value exceeding the calculated value. Thus, from the data given in Table 2 we calculated that the percentage of hydrogen-bonded amide groupings is about 67.21, whereas the first scheme for the disposition of the macromolecules will permit hydrogen bonding only to the extent of 50% or less.

Unlike this system, the system HAz–HG, molar ratio 1 : 1, cannot assume a state in which the disposition of the macromolecules permits hydrogen bonding to the extent of more than 50%. Below we show one of the possible arrangements of the macromolecules of this polyamide, from which it will be seen that in this case 50% of the amide groupings may be hydrogen-bonded:



The same result is obtained when other arrangements of the macromolecules are considered. The percentage of hydrogen-bonded amide groupings calculated from the melting point is 51.87.

The relationship that we have shown to exist between the mutual disposition of the macromolecules of mixed polyamides and the extent of hydrogen bonding provides a basis for an explanation of the strengthening process that occurs during the cold drawing of these materials. During this process the material flows, so that the macromolecules move relative to one another. It then becomes possible for macromolecules to take up positions in which the intermolecular hydrogen bonding is at a maximum. The macromolecules will become fixed in these mutual positions within the mass of the polyamide. This disposition of the macromolecules corresponds to the moment when the polyamide sample acquires maximum mechanical strength. It is natural that the process of drawing will be accompanied by the straightening of the macromolecules and will result in an oriented arrangement of macromolecules within the materials, which is the main result of this process.

SUMMARY

1. A study was made of binary mixed polyamides derived from 1,6-hexanediamine glutarate or pimelate as one component and 1,6-hexanediamine adipate, azelaate, or sebacate as the other component of the reacting mixture.

2. It was found that the investigated systems had minimum melting points for a content of 60 mole-% of the component having an odd number of carbon atoms in its molecule.

3. The question was considered of the effect of the mutual disposition of the polyamide macromolecules on the extent of the hydrogen bonding of the amide groupings, and it was shown that the extent of hydrogen bonding varies greatly with variation in the mutual dispositions of the macromolecules of mixed polyamides.

4. An explanation was advanced for the occurrence of a minimum on the curve for melting point against composition.

5. It was suggested that the extent of hydrogen bonding in mixed polyamides may change as a result of cold drawing.

LITERATURE CITED

[1] V. V. Korshak and T. M. Frunze, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, No. 1, 163 (T.p. 143)*.

[2] V. V. Korshak and T. M. Frunze, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, No. 2, 372 (T.p. 333)*.

[3] D. Vogel, J. Chem. Soc., 1929, 726; B. Kerr, J. Am. Chem. Soc., 51, 617 (1929).

[4] A. Verkade, C. Hartman, J. Coops Rec. trav. chim., 45, 380.

[5] R. Hill, E. Walker, J. Polymer Sci., 3, 609 (1949).

[6] V. V. Korshak and T. M. Frunze, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, No. 4, 762 (T.p. 679)*.

[7] V. V. Korshak and T. M. Frunze, Proc. Acad. Sci. USSR, 97, 261 (1954).

[8] V. V. Korshak and T. M. Frunze, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, No. 3, 563; 1955, No. 2, 372 (T.p. 499, 333)*.

---

* T.p. = C. B. Translation pagination

Received May 19, 1955

Institute of Heteroorganic Compounds of the
USSR Academy of Sciences

MACROMOLECULAR COMPOUNDS

COMMUNICATION 82. 2,4,5-TRIISOPROPYL-α-METHYLSTYRENE

V. V. Korshak and N. G. Matveeva

As shown previously, substituents on carbon atoms linked by a double bond have a hindering effect on the polymerization process, this effect being particularly great when there are numerous bulky subhtituents [1-5]. The obstacles to the polymerization process are particularly great when four or three substituents are present [6]. However, the presence of only one substituent, if it is bulky and appreciably ramified, is sometimes sufficient to cause great hindrance to the polymerization process. Thus, it was found that 4-tert-butyl-2,6-dimethylstyrene is unable to undergo radical polymerization, though it is still able to polymerize in presence of catalysts acting by the ionic mechanism [7, 8]. When there is only one substituent in the ortho position of the phenyl group the steric hindrance is not so great, as we showed in the case of 2,4,5-triisopropylstyrene, which readily polymerizes, both under the action of initiators and also simply by the action of heat [9].

It was of interest to determine the effect of a substituent such as a methyl group when it is not in the phenyl group but is directly substituted in the vinyl group. There are references to the behavior of such compounds in the literature. It is known, for example, that α-methylstyrene does not readily polymerize by the radical mechanism, though it undergoes ionic polymerization as readily as styrene itself. Bachman and Hellman [10] found that α, 2,3-trimethylstyrene does not polymerize in presence of peroxides, but its ability to undergo ionic polymerization was not examined.

When there are two ortho substituents in the phenyl group and one substituent in the vinyl group, then, as we showed for 4-tert-butyl-α, 2,6-trimethylstyrene and 2,6-dimethoxy-α-methylstyrene, the compounds are not capable of either radical or ionic polymerization. Hence, the presence of two ortho substituents in the phenyl group and one α-substituent in the vinyl group creates great steric hindrance, blocking and screening the vinyl group to such an extent that it loses its ability to react with the similar group of another molecule.

It was of interest to determine the effect of a single ortho substituent in α-methylstyrene for the case in which this substituent is fairly bulky, like the isopropyl group. With this object we synthesized 2,4,5-triisopropyl-α-methylstyrene. The starting material for the synthesis was 2', 4', 5'-triisopropylacetophenone, which was prepared from 1,2,4-triisopropylbenzene and acetyl chloride in presence of aluminum chloride in 62.1% yield. The 2', 4', 5'-triisoprophylacetophenone was then treated with the Grignard reagent derived from methyl iodide, but it was not found possible to introduce a methyl group in this way. Shorygin's method was then tried, and this was successful. The 2', 4', 5'-triisopropylacetophenone was treated with sodium and methyl iodide, and vacuum distillation without isolation of the intermediate product yielded 2,4,5-triisopropyl-α-methylstyrene, a colorless mobile liquid having a powerful aromatic odor and boiling at 110-111° (5 mm).

2,4,5-Triisopropyl-α-methylstyrene did not polymerize when heated at 100° for 100 hours in presence of benzoyl peroxide and when heated at 160° for 50 hours in absence of benzoyl peroxide. After treatment in this way, the original substance was recovered unchanged. Ionic catalysts were tried, also without success – after treatment in presence of aluminum chloride (1% on the amount of 2,4,5-triisopropyl-α-methylstyrene), the original monomer was recovered unchanged.

The absence of ability to undergo radical and ionic polymerization indicates that in 2,4,5-triisopyl-α-methylstyrene large steric effects operate and prevent the mutual approach of two vinyl groups which is necessary for reaction to occur. These steric-hindrance effects – or steric factors – in this case evidently include both a screening effect, and also a blocking effect, which is exerted by the two substituents on the double bond of the vinyl group.

In 4-tert-butyl-2,6-dimethylstyrene, which we investigated previously, there are two methyl groups ortho to the vinyl group, and the resulting blocking of the double bond led to loss in ability to polymerize by the radical mechanism, while the ability to polymerize in presence of ionic catalysts remained, ionic polymerization being much less sensitive to the action of steric hindrance – as we have shown previously [6, 7].

Hence, a small substituent, such as a methyl group, when directly attached to the doubly-bond carbon, has a greater inhibiting effect on the polymerization process than two similar groups in the ortho positions of the phenyl group of the substituted styrene.

EXPERIMENTAL

2', 4', 5'-Triisopropylacetophenone. Aluminum chloride (25 g) was added in small portions to a cooled stirred mixture of 30 g of 1,2,4-triisopropylbenzene, 15 g of acetyl chloride, and 100 ml of tetrachloroethane. The mixture was set aside overnight, heated in a water bath for one hour, and poured into dilute hydrochloric acid to effect decomposition. The organic layer was separated in a separating funnel, and then washed – first with water, then with dilute sodium carbonate solution, and finally several times with water. The washed solution was dried with sodium sulfate, tetrachloroethane was distilled off, and the residue was vacuum-distilled. The fraction boiling at 156-162° (25 mm) was collected and recrystallized from alcohol; the yield was 22.5 g (62.1%).

2', 4', 5'-Triisopropylacetophenone forms long white needles having sharp odor of frankincense. It melts at 106-107° [9].

2,4,5-Triisopropyl-α-methylstyrene. A mixture of 20 g of 2', 4', 5'-triisopropylacetophenone, 40 g of methyl iodide, 18 g of granular sodium, and 200 ml of ether was prepared in a round-bottomed flask fitted with reflux condenser. As reaction was very slow, 1 ml of ethanol was added, and the reaction then became fairly vigorous. When the reaction slowed down, the flask was heated in a water bath for 60-90 minutes. The ether layer and suspended sodium derivative was decanted from the sodium. The mixture of sodium and sodium derivative that remained was shaken several times with ether, and the suspension of sodium derivative in ether was decanted; in this way the whole of the sodium derivative was extracted. The ether extracts were combined, and the sodium derivative was decomposed with water. The ether layer was separated in a separating funnel and washed – first with water, then with dilute hydrochloric acid, and finally several times with water. The ethereal solution was dried with anhydrous sodium sulfate, and the ether was distilled off. The residue was vacuum-distilled, and the fraction boiling at 114-118° (6 mm) was collected.

2,4,5-Triisopropyl-α-methylstyrene is a colorless highly mobile liquid having a fairly strong aromatic odor and boiling at 110-111° (5 mm). It is readily soluble in organic solvents and is insoluble in water. It has d_4^{20} 0.863; n_D^{20} 1.4870; Found MR 81.37; Calculated MR 81.26.

SUMMARY

1. 2,4,5-Triisopropyl-α-methylstyrene was synthesized.
2. It was found that 2,4,5-triisopropyl-α-methylstyrene will undergo neither radical nor ionic polymerization.

LITERATURE CITED

[1] V. V. Korshak, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1949, 269.

[2] V. V. Korshak and N. G. Matveeva, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953 No. 3, 542 (T.p. 487)*.

[3] V. V. Korshak and N. G. Matveeva, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, No. 4, 751 (T.p. 675)*.

[4] V. V. Korshak, Chemistry of Macromolecular Compounds, Acad. Sci. USSR Press, 1950, p. 180.

[5] V. V. Korshak and N. G. Matveeva, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, No. 6, 1116 (T.p. 991)*.

[6] V. V. Korshak and N. G. Matveeva, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, No. 2, 344 (T.p. 313)*.

[7] V. V. Korshak and N. G. Matveeva, Proc. Acad. Sci. USSR, 85, 797 (1952).

[8] V. V. Korshak and N. G. Matveeva, J. Gen. Chem., 22, 1173 (1952) (T.p. 1221)*.

[9] V. V. Korshak and N. G. Matveeva, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, 547 (T.p. 491)*.

[10] G. B. Bachman, H. M. Hellman, J. Am. Chem. Soc., 70, 1772 (1948).

Received July 8, 1954

Institute of Heteroganic Compounds of the
USSR Academy of Sciences

---

* T.p. = C. B. Translation pagination

BRIEF COMMUNICATIONS

PREPARATION OF p-TERPHENYL

B. M. Mikhailov and P. M. Aronovich

The known methods for the synthesis of p-terphenyl do not give the completely pure hydrocarbon in satisfactory yield – either they give high yields of inadequately pure hydrocarbon, or they give the pure substance, but in very low yield. For example, p-terphenyl can be prepared in 70% yield by the condensation of N,N'-p-phenylenebis[N-nitroacetamide] with benzene [1], but the product, after distillation at 0.001 mm and crystallization, has a low melting point. According to Braun [2], an almost quantitative yield of terphenyl can be attained by heating p-dicyclohexylbenzene with bromine. However, even after crystallization from benzene and distillation over sodium, the product melts at 209°. Dehydrogenation and simultaneous dehydration of 1,4-diphenyl-1,4-cyclohexanediol in presence of selenium [3] also gives inadequately pure p-terphenyl – after repeated sublimation in a high vacuum the substance melts at 210°.

Pure p-terphenyl (m.p. 213°) was prepared by Basford [4] by the dehydrogenation of 4-cyclohexylbiphenyl with selenium, but the author gives no indication of the yield. Dehydrogenation and decarboxylation of 3,6-diphenyl-4-cyclohexene-1,2-dicarboxylic anhydride (prepared by the condensation of 1,4-diphenyl-1,3-butadiene with maleic anhydride) [5] also gives the pure hydrocarbon (m.p. 211.5-212.5°), but in low yield.

We have worked out a method for the preparation of p-terphenyl by the dehydrogenation of p-dicyclohexylbenzene with selenium, and this enables us to obtain p-terphenyl of high purity in 66% yield. Since dehydrogenation with selenium proceeds only at the interface between the layers, the reaction rate can be considerably increased by agitation of the mixture. However, even then, reaction is rather slow. When a mixture of p-dicyclohexylbenzene and selenium was heated at 320° for 100 hours, the yield of p-terphenyl after a single crystallization from benzene was 73% (m.p. 210-212°). The product had a grayish tinge owing to admixture of colloidal selenium; it was purified quite readily by chromatography of its benzene solution on alumina. The resulting hydrocarbon formed completely colorless crystals, m.p. 212-213°.

In the procedure described below, in order to reduce the amount of solvent required it is recommended that the chromatography should be carried out on the hot benzene solution. However, the chromatography can be carried out on cold benzene solutions and also on solutions of p-terphenyl in other solvents, such as carbon tetrachloride.

EXPERIMENTAL

The dehydrogenation of p-dicyclohexylbenzene – which was prepared by Corson and Ipatieff's method [6] – was carried out in a long-necked round-bottomed flask or wide stainless-steel vessel. The neck of the flask or opening of the steel vessel was closed by a stopper carrying a two-way adapter. The side tube of the adapter was connected to an Ivitsky vessel containing caustic potash solution (for the absorption of hydrogen selenide). A stirrer passed through the vertical tube of the adapter. A mixture of 50 g (0.21 mole) of p-dicyclohexylbenzene (m.p. 97-99°) and 100 g (1.27 g-atoms) of selenium was prepared in the reaction vessel. The vessel was placed in a bath of Wood's metal, the bath was heated to 320°, and the stirrer was set in motion. The mixture was stirred at a bath temperature of 320-330° for 90-100 hours (with some interruptions), and a test sample was then taken from the upper layer of the reaction mixture. The sample was dissolved in hot benzene, the resulting solution was filtered, the filtrate was evaporated to dryness, and the melting point of the residue was determined. In such a test, reaction can be regarded as substantially complete when the sample melts completely at not below 203° (corrected).

When reaction was complete, the hot mixture was poured into a porcelain basin (in a fume cupboard!). When it was cool, it was ground and boiled with 800 ml of benzene. The hot solution was filtered through a heated Buchner funnel; unchanged selenium (about 20 g) remained on the filter (such selenium can be used in further experiments). The p-terphenyl that precipitated when the solution cooled was filtered off and washed with 20 ml of benzene. It was pressed off (a dried sample melted at 210-212°) and dissolved in 1100 ml of boiling benzene. The resulting solution was chromatographed on 100 g of active alumina. In order to prevent the crystallization of the p-terphenyl during the chromatography process, the column was fitted with a hot-water jacket, which was maintained at 65-70°. When the p-terphenyl solution had passed through, the column was washed twice with hot benzene (about 100 ml), and the liquid passing through was collected in the receiver containing the main solution. One-half of the solvent was distilled from the mixture of crystals and solution, and the residue was cooled and filtered. The precipitate was washed three times with 20-ml portions of benzene and dried. The product, amounting to 31.5-32 g (65-66%), consisted of white crystals, m.p. 212-213°.

SUMMARY

A method has been developed for the preparation of pure p-terphenyl.

LITERATURE CITED

[1] H. France, J. M Heilbron, D. H. Hey, J. Chem. Soc. 1938, 1364; 1940, 369; U.S. Pat., 2301206, 1943; C. A. 37, 2019; Cf. "Organic Reactions", 1950, p. 272.

[2] J. Braun, Ber., 60, 1180 (1927).

[3] E. Muller, G. Sok, 70, 1990 (1937).

[4] R. Basford, J. Chem. Soc., 1936, 1593.

[5] R. Kuhn, Th. Wagner-Jauregg, Ber., 63, 2662 (1930).

[6] B. B. Corson, V. M. Ipatieff, J. Am. Chem. Soc., 59, 645 (1937).

Received May 3, 1955

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

ORGANOBORON COMPOUNDS

COMMUNICATION 3. PREPARATION OF THE ISOBUTYL ESTERS OF PHENYLPROPYL - AND BUTYLPHENYL BORINIC ACIDS

B. M. Mikhailov and P. M. Aronovich

By the action of phenyllithium on diisobutyl benzeneboronate, we prepared isobutyl diphenylborinate in 71% yield. Further study of the reaction between esters of benzeneboronic acid and other organoboron compounds showed that these reactions permit the preparation of previously undescribed alkylarylborinic esters. For example, by the action of propyllithium and of butyllithium on diisobutyl benzeneboronate, the isobutyl esters of phenylpropyl – and butylphenylborinic acids were prepared. These esters, like those of dibutylborinic [1] and diphenylborinic [2] acids, are difficult to hydrolyze. In the air they rapidly undergo change, being converted into benzeneboronic acid: it is evident that oxidation occurs and is accompanied by the hydrolysis of the benzeneboronic ester formed.

EXPERIMENTAL

Isobutyl Phenylpropylborinate. At – 50° to – 70° 46.8 g (0.2 mole) of diisobutyl benzeneboronate, diluted with 50 ml of ether, was added with stirring over a period of 30-40 minutes to a solution of propyllithium prepared at 0° from 32 g of propyl bromide, 3.5 g of lithium, and 200 ml of ether. The mixture was stirred for five hours at -70°, and then set aside overnight. On the next day the solution, which contained a little white precipitate, was saturated with dry hydrogen chloride. The greater part of the ether was distilled off, and the precipitate of lithium chloride and bromide was filtered off.

The precipitate was washed with 15 ml of benzene, and solvent and isobutyl alcohol were distilled from the filtrate under reduced pressure at temperatures up to 50-60°. Lithium salts were again filtered off, and the liquid was vacuum-fractionated through a column. The yield of isobutyl phenylpropylborinate, b.p. 87-90° (3 mm), was 22.8 g (55.8%). After a second distillation the ester boiled at 86-87° (3 mm) and had d_4^{20} 0.8943.

Found %: C 76.53; H 10.12; B 5.27
$C_{13}H_{21}OB$. Calculated %: C 76.49; H 10.37; B 5.30

Iosbutyl Butylphenylborinate. Reaction was between 0.2 mole of diisobutyl benzeneboronate and 0.2 mole of butyllithium, the conditions being as described above. The yield of isobutyl butylphenylborinate, b.p. 96-97° (3 mm) and d_4^{20} 0.8894, was 29.4 g (67.4%).

Found %: C 77.03; H 10.64; B 4.63
$C_{14}H_{23}OB$. Calculated %: C 77.07; H 10.62; B 4.96

The syntheses of these esters were carried out in an atmosphere of dry nitrogen.

SUMMARY

It is shown that it is possible to prepare esters of mixed alkylarylborinic acids.

LITERATURE CITED

[1] J. R. Johnson, H. R. Snyder, M. G. Van Campen, J. Am. Chem. Soc., 60, 115 (1938).

[2] B. M. Mikhailov and V. A. Vaver, Proc. Acad. Sci. USSR, 102, 531 (1955).

Received May 30, 1955

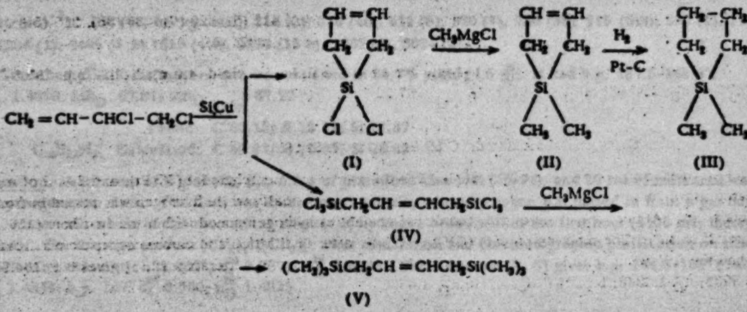
N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

SYNTHESIS OF 1,1-DICHLOROSILACYCLOPENT-3-ENE

A. D. Petrov, G. I. Nikishin, N. P. Smetankina, and Yu. P. Egorov

There have been no reports of the preparation of unsaturated cyclic compounds containing a silicon atom and a double bond in the ring. All of the known saturated 4-, 5-, 6-, and 7-membered ring compounds containing silicon in the ring have been prepared by organometallic synthesis [1-6], with the exception of the trisilacyclohexane derivative of formula $[CH_2-SiCl_2]_3$, formed by the reaction of CH_2Cl_2 with silicon [7].

In a study of the behavior of 3,4-dichloro-1-butene in the direct synthesis, we found that in addition to 1,1,1,6,6,6-hexachloro-1,6-disilahex-3-ene (IV) the unsaturated heterocyclic compound 1,1-dichlorosilacyclopent-3-ene (I) was formed (the compounds are named in accordance with the Amsterdam nomenclature [8]. The formation of these compounds was evidently preceded by allyl rearrangement of 3,4-dichloro-1-butene to 1,4-dichloro-2-butene:



The structures of (II), (III), and (V) were confirmed by their Raman spectra. Thus, in the spectrum of (III) the following intense lines were found: 399 (5), 598 (10), 852 (4sh), 945 (2), 1022 (2), 1252 (3) cm^{-1} which coincide with the frequencies for 1,1-dimethylsilacyclopentane, which has been determined previously [2]. The spectrum of (II) contains a few intense lines, which may indicate the symmetrical character of its structure. The frequency of 915 cm^{-1} is probably an analog of symmetrical pulsational vibration of the ring [at 852 cm^{-1} in (III)]. An increase in frequency is observed also in alicyclic compounds: cyclopentane 886 cm^{-1}, cyclopentene 896 cm^{-1}. The C=C frequency (1610 cm^{-1}) is very close for that of the double bond in cyclopentene (1611 cm^{-1}). In the spectrum of (V) the C=C frequency is 1650 cm^{-1}, i. e. is higher than when the bond is in the α,β-position with respect to the silicon (1630 cm^{-1}). This fact, and also the absence of frequencies in the region of 3000-3100 cm^{-1}, attributable to a $=CH_2$ group, favors the structure (V) rather than $(CH_3)_3SiCH_2CH-\underset{\displaystyle Si(CH_3)_3}{\underset{|}{C}H}=CH_2$. It is interesting to note that among the products of direct synthesis from 1,4-dichloro-2-butene, the compound (I) was again found, though in smaller amount.

EXPERIMENTAL

Direct Synthesis. A stream of 3,4-dichloro-1-butene (416 g) was passed at the rate of 23 g per hour through a glass tube (d = 40 mm, l = 600 mm) filled with pieces of Si−Cu alloy (Si~ 80%; Cu~ 20%) and placed in an electric tube furnace working at a temperature of 300 ± 10°. The product (280 g) was condensed by means of a water condenser and was then fractionated. Two fractions were obtained: 43.6 g (15.6%) of Fraction I, b.p. 128-136°, corresponding to 1,1-dichlorosilacyclopent-3-ene, b.p. 135°, d_4^{20} 1.2190; n_D^{20} 1.4782; MR_D 35.56; $MR_{D_{calc.}}$ 36.2

Found: C 30.42; H 3.96; Cl 47.65; Si 17.95

$C_4H_6SiCl_2$. Calculated: C 31.37; H 3.95; Cl 46.32; Si 18.35

and 25 g (9%) of Fraction II, b.p. 240-243°, corresponding to 1,1,1,6,6,6-hexachloro-1,6-disilahex-3-ene, b.p. 243 d_4^{20} 1.4115, n_D^{20} 1.4879; MR_D 65.92; $MR_{D\,calc.}$ 65.00

Found: C 15.40; H 2.16; Cl 65.76; Si 17.24

$C_4H_6Si_2Cl_6$. Calculated: C 14.87; H 1.87; Cl 65.86; Si 17.39

Replacement of Chlorine by Methyl in the direct-synthesis products was effected with aid of CH_3MgCl. To the stirred ethereal solution of the Grignard reagent, which was prepared from 19.3 g (0.82 mole) of magnesium and 14.2 g (0.582 mole) of methyl chloride, the direct-synthesis product (I) or (IV) was added, the amounts taken being 33.1 g (0.176 mole) of (I) and 21 g (0.065 mole) of IV) *. After the reactants had been mixed, the reaction mixtures were boiled for 9-10 hours, and the products were isolated in the usual way.

The yield of 1,1-dimethylsilacyclopent-3-ene was 9.72 g (39.4%), and it had b.p. 100.5-101° (741-744 mm); d_4^{20} 0.8067; n_D^{20} 1.4433; MR_D 36.91; $MR_{D\,calc.}$ 36.94

Found: C 63.81; H 10.91; Si 24.76

$C_6H_{12}Si$. Calculated: C 64.2; H 10.78; Si 25.02

Raman spectrum (cm^{-1}): 183 (4b, background), 214 (2), 310 (4b), 411 (5), 620 (7), 730 (3b), 915 (5sh), 950 (1), 1100 (4), 1206 (4), 1258 (1), 1405 (5 b) 1610 (4 sh), 2894 (10 b), 2965 (8), 3024 (5).

1,1,8,8-Tetramethyl-2,7-disilaoct-4-ene was obtained in 34.7% yield (4.5 g); it had b.p. 187.5-188.5°; d_4^{20} 0.7789; n_D^{20} 1.4398; MR_D 67.81; $MR_{D\,calc.}$ 67.22

Found: C 60.15; H 12.12; Si 27.87

$C_{10}H_{24}Si_2$. Calculated: C 59.91; H 12.07; Si 28.02

Hydrogenation. A mixture of 6 g of (II), 0.1-0.2 g of platinized charcoal (5% Pt), and 20 ml of methanol was prepared in a hydrogenation flask. The flask was shaken mechanically while hydrogen was passed in from a gas holder for four hours. Almost the whole of the theoretical amount of hydrogen added within the first hour (1100 ml; theory requires 1200 ml). The reaction product $(CH_2)_4Si(CH_3)_2$, after distillation and chromatographic purification on silica gel, had the following constants: b.p. 107°, d_4^{20} 0.7871; n_D^{20} 1.4328. The literature [2, 5] gives b.p. 104.9-105° (742 mm); d_4^{20} 0.7938; n_D^{20} 1.4348; b.p. 107° d_4^{25} 0.780; n_D^{25} 1.4335.

SUMMARY

It is shown that, in direct synthesis from 3,4-dichloro-1-butene, not only 1,1,1,6,6,6-hexachloro-1,6-disilahex-3-ene, but also 1,1-dichlorosilacyclopent-3-ene may be formed.

LITERATURE CITED

[1] A. Bygden, Ber., 48, 1236 (1915).

[2] A. F. Plate, N. A. Momma, and Yu. P. Egorov, Proc. Acad. Sci. USSR, 97, 847 (1954).

[3] Makoto Kumada, J. Inst. Polytech., Osaka City, Univ. Ser. C., No. 1, 11-18 (1951); C. A., 46, 6083 (1952).

[4] R. West, E. Rochow, Naturwissenschaften, 40, 142 (1953).

[5] R. West, J. Am. Chem. Soc., 76, 6012 (1954).

[6] L. H. Sommer, S. Baum J. Am. Chem. Soc., 76, 5002 (1954).

[7] A. D. Petrov and V. A. Ponomarenko, Proc. Acad. Sci. USSR, 90, No. 3, 387 (1953).

---

* The amounts are given as in the original text, but calculation shows that there are considerable discrepancies between the weights in grams and the corresponding molar quantities. – Publisher.

[8] M. G. Voronkov and B. N. Dolgov, Sci. Memoirs Leningrad State Univ., Chemical Series, No. 11, 80 (1952).

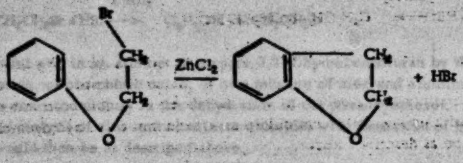
Received May 4, 1955

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

REACTIONS OF 2-BROMOETHYL PHENYL ETHER IN PRESENCE OF ZINC CHLORIDE AND A MIXTURE OF ZINC AND ALUMINUM CHLORIDES

E. N. Karaulova and G. D. Galpern

Rindfuss [1] described the synthesis of 2,3-dihydrobenzofuran (II) by the cyclization of 2-phenoxyethanol, and also of 2-bromoethyl phenyl ether (I), in presence of zinc chloride:



(I) (II)

The apparent simplicity of this synthesis attracted our attention. Repetition of the described synthesis yielded a product of b.p. 87-90° (17.5 mm) and $n_D^{25.5}$ 1.542 [for 2,3-dihydrobenzofuran Rindfuss gives b.p. 88-90° (18 mm) and n_D^{20} 1.543]. However, further investigation showed that the product was not 2,3-dihydrobenzofuran, but phenol. Such physicochemical characteristics as boiling point, refractive index, and density are very similar for unpurified moist phenol and for 2,3-dihydrobenzofuran (the difficulty of preparing phenol in a high degree of purity is well known). Both 2,3-dihydrobenzofuran and phenol give violet colors with ferric chloride in presence of sulfuric acid. 2,3-Dihydrobenzofuran differs considerably from phenol in elementary composition, but, unfortunately, Rindfuss does not give the 2,3-dihydrobenzofuran.

EXPERIMENTAL

We took a mixture of 76.6 g of the ether (I) and 8 g of freshly fused, finely ground zinc chloride and refluxed it for two hours. Hydrogen bromide was evolved slowly and the boiling point (thermometer in the mixture) fell from 220° to 200°. The reaction products were vacuum-distilled (there was a very small amount of resinous residue). The distillate was washed with water and with 10% caustic soda solution, and was then dried and redistilled, three fractions being collected:

Fraction I, b.p. 51° (34 mm), 90° (26 mm); yield 10.51 g. Redistillation at atmospheric pressure yielded 6.4 g of a substance having b.p. 129-134° and $n_D^{26.4}$ 1.5378. The bromine content was 82.36%, and the value calculated for $C_2H_4Br_2$ is 83.57% (the dibromoethane contained some phenol impurity).

Fraction II, b.p. 83-90° (17.5 mm) – mainly 87-90° (17.5 mm); yield 7.87 g. Redistillation at atmospheric pressure gave a product boiling at 181-185° and having $n_D^{22.6}$ 1.542. When allowed to stand it crystallized and was found to melt at 39°. It was distilled once more and analyzed.

Found %: C 76.43; H 6.48
C_6H_6O. Calculated %: C 76.59; H 6.38

Fraction III, b.p. 210-230° (21 mm); m.p. 34.5°; yield 17.50 g. This was identified by a mixture melting point test as unchanged ether (I).

When, in similar experiments, the reaction mixture was refluxed for five hours, its boiling point continued to fall, and finally attained 155°, the boiling point of phenyl vinyl ether. When heating was continued still further the whole mass polymerized and there was extensive resinification. Further experiments with zinc chloride of various origins and with mixture of zinc and aluminum chlorides gave qualitatively the same results.

The greatest amount of phenol was formed when the ether (I) reacted in presence of equal amounts of zinc chloride and aluminum chloride (containing ferric chloride impurity). A mixture of 40.6 g of the ether 1.4 g of zinc chloride, and 4 g of aluminum chloride was heated for 2 hours 30 minutes and then treated as described above. The products were dibromoethane (3.66 g), phenol (7.68 g), and unchanged ether (I) (7.88 g). In none of the experiments did we succeed in detecting the presence of 2,3-dihydrobenzofuran among the products.

The results that we have obtained can be epplained on the assumption that hydrogen bromide is first eliminated from the ether (I) when this is heated with zinc chloride (or its mixture with aluminum chloride):

$$C_6H_5OCH_2CH_2Br \xrightarrow[HBr]{ZnCl_2} C_6H_5OCH=CH_2 \rightarrow (C_6H_5OCH=CH_2)_n + HBr$$

At the high temperature the resulting phenyl vinyl ether rapidly polymerizes. In presence of zinc chloride the unchanged ether (I) reacts with hydrogen bromide.

$$C_6H_5OCH_2CH_2Br + HBr \xrightarrow{ZnCl_2} C_6H_5OH + BrCH_2CH_2Br.$$

We were unsuccessful also in an attempt to prepare 2,3-dihydrobenzofuran by the cyclization of 2-phenoxyethanol in presence of zinc chloride, of phosphoric oxide, or of a mixture of zinc and aluminum chlorides. It appeared that the first stage of the process consisted mainly in the dehydration of the phenoxyethanol. The water eliminated would then bring about the partial hydrolysis of zinc and aluminum chlorides with formation of hydrogen chloride. The further course of the reaction would then be as described above.

SUMMARY

When 2-bromoethyl phenyl ether was heated with zinc and aluminum chlorides, phenol and dibromoethane were formed, and apparently also phenyl vinyl ether and its polymers.

Contrary to Rindfuss' view, 2,3-dihydrobenzofuran is not formed under these conditions; nor is it formed when 2-phenoxyethanol is heated with zinc chloride, with phosphoric oxide, or with a mixture of zinc and aluminum chlorides.

LITERATURE CITED

[1] R. E. Rindfuss, J. Am. Chem. Soc. 41, 665 (1919).

Received April 21, 1955

Petroleum Institute of the USSR Academy
of Sciences

CHLORINATION OF DODECANE *

V. A. Nekrasova and N. I. Shuikin

The object of this investigation was to determine the conditions required in the synthesis of chloro derivatives of dodecane. The experiments were carried out in the apparatus described in our previous communication on the chlorination of undecane [1].

There is very little information in the literature on the chlorination of dodecane. Mabery [2] chlorinated dodecane in diffused light: the monochlorododecane that he obtained boiled over a wide range, 142-153° (80 mm), and he regarded the fraction boiling at 150-160° (80 mm) as dichlorododecane. The yields of the chloro derivatives were not given.

EXPERIMENTAL

As starting material for the preparation of chloro devivatives of dodecane we used the ligroin fraction of straight-run Crimean petroleum. Normal hydrocarbons were separated from their isomers and from cyclic hydrocarbons via the urea complex [3], and they were then subjected to precision fractionation. The isolated dodecane had the following properties: b.p. 215.5-217° (755 mm); d_4^{20} 0.7489; n_D^{20} 1.4218. Dodecane for use in control experiments (372 g) was synthesized from hexyl bromide by the Wurtz method, and its properties were as follows: b.p. 216-217° (758 mm); d_4^{20} 0.7487; n_D^{20} 1.4216; found MR 57.76; calculated $C_{12}H_{26}$ MR 57.62.

The chlorination of dodecane was carried out – both in vapor phase and in liquid phase – in presence of nitrogen dioxide. The molar ratio of dodecane and chlorine was 1 : 1 in all experiments, and chlorine was supplied at 1200 ml per hour. By way of example we shall describe beiefly the results of the fractionation of the products obtained in an experiment on the vapor-phase chlorination of dodecane. At the above-stated molar ratio of reactants and rate of passage of chlorine, 85 g of dodecane was chlorinated at 400° and 83 g of chlorination product was obtained. The product was fractionated, and yielded:

Fraction I, B.p. 243-245° (758 mm); 37.0 g (44.6%); n_D^{20} 1.4380; d_4^{20} 0.8614; Cl 17.49%

Fraction II, B.p. 255-257° (758 mm); 23.7 g (28.5%); n_D^{20} 1.4425; d_4^{20} 0.8670; Cl 17.43%;

Found MR 62.47; calculated for $C_{12}H_{25}Cl$ MR 62.48

Fraction III, B.p. 257-259°; 17.4 g (21%)

Residue 4.9 g (5.9%).

Comparison of the constants with reported values [4] indicated that Fraction I consisted of secondary monochloro derivatives; Fraction II corresponded to 1-chlorododecane; and Fraction III corresponded to a mixture of dichloro derivatives. The structure of the primary monochlorododecane was established by its hydrolysis to dodecyl alcohol (b.p. 256-257° at 758 mm) [5], which was converted by oxidation with alkaline hydrogen peroxide into lauric acid:

$$CH_3(CH_2)_{10}CH_2Cl \rightarrow CH_3(CH_2)_{10}CH_2OH \rightarrow C_{11}H_{23}COOH.$$

The acid so obtained melted at 44.3° and boiled at 223-224° (99-100 mm); these constants are close to the reported values [6]. The results of the vapor-phase chlorination of dodecane at various temperatures are given in the table.

At 420° the vapor phase chlorination of dodecane resulted in much decomposition and the formation of a charred residue.

We considered it desirable to study also the liquid-phase chlorination of dodecane in presence of a small amount

---

* Senior laboratory worker Z. V. Popova took part in the experimental work.

of nitrogen dioxide (2% on the weight of hydrocarbon) at a temperature close to the boiling point of the hydrocarbon (215-216°), chlorine being passed into the flask containing liquid dodecane at the rate of 1200 ml per hour. By way of example we shall give the results of the fractionation of the chlorination products obtained in one experiment. Under the conditions indicated above 85 g of dodecane yielded 99.7 g of chloro derivatives. Fractionation at 756 mm gave the following fractions:

Fraction I. B.p. 243-245°; 44.9 g (45%); n_D^{20} 1.4380; d_4^{20} 0.8614; Cl 17.49%

Fraction II. B.p. 255-257°; 10.9 g (18%); n_4^{20} 1.4425; d_4^{20} 0.8670; Cl 17.43%

Fraction III. B.p. 257-259°; 29.9 g (30%)

Residue 6.98 g (7%).

TABLE

Vapor-phase Chlorination of Dodecane in Presence of Nitrogen Dioxide

Expt. No.	Experimental temperature (°C)	Yield (%) on the amount of dodecane that reacted			
		1-Chlorododecane	Secondary monochlorododecanes	Dichloro derivatives	Residue
4	390	27.3	46.2	20.8	5.7
7	400	28.5	44.6	21.0	5.9
11	410	28.2	44.3	21.5	6.0
14	420	25.4	42.5	24.3	9.8

Fraction I corresponded in properties to secondary monochloro derivatives; Fraction II was 1-chlorododecane; Fraction III was a mixture of dichloro derivatives; and the residue apparently consisted of higher chlorination products.

An examination of our results on the liquid- and vapor-phase chlorination of dodecane indicates that it is most expedient to carry out the chlorination (not only of this hydrocarbon, but also of most other hydrocarbons of higher molecular weight) in the liquid phase in presence of nitrogen dioxide, since at high temperatures of 420° and higher the chloro derivatives formed undergo rapid decomposition under the conditions of vapor-phase chlorination. The presence of small amounts (2%) of nitrogen dioxide in the reaction mixture facilitates the initiation of the chain reaction – the formation of a free dodecyl radical in accordance with the scheme that we proposed in the preceding communication [1].

SUMMARY

1. The reaction of dodecane with chlorine in presence of nitrogen dioxide at high temperature (390-420°) was studied.

2. The optimum conditions were found for the formation of 1-chlorododecane in the vapor and liquid phases in presence of nitrogen dioxide.

3. In the chlorination of hydrocarbons containing 12 or more carbon atoms at 420°, it is desirable to carry out the reaction in the liquid phase in presence of nitrogen dioxide.

LITERATURE CITED

[1] V. A. Nekrasova and N. I. Shuikin, Proc. Acad. Sci. USSR, 97, 843 (1954).

[2] C. F. Maberry, Am. Chem. J., 19, 419, 482 (1897).

[3] W. Z. Zimmerschied, R. A. Dinerstein, Ind. Eng. Chem., 42, 1300 (1950).

[4] A. J. Vogel, J. Chem. Soc., 1943, No. 12, 641.

[5] H. Adkins, K. Folkers, J. Am. Chem. Soc., 53, 1096 (1931).

[6] J. Timmermans, Physico-Chemical Constants of Pure Organic Compounds, New York, 1950, p. 398.

Received June 3, 1955

N. D. Zelinsky Institute of Organic
Chemistry of the USSR Academy of Sciences

CATALYTIC DEHYDROGENATION OF ISOPENTANE

N. I. Shuikin, T. P. Dobrynina, E. A. Timofeeva, and Yu. P. Egorov

The considerable amounts of pentane and isopentane that are available from the petroleum industry make it necessary to consider the question of their rational utilization. In previous papers [1, 2] we gave some results on the dehydrogenation of pentane: we showed that treatment of pentane at 500-550° can yield catalyzates containing 22-26% of pentenes. The object of the present investigation was to find the conditions under which isopentenes are obtained in the catalytic dehydrogenation of isopentane, and to determine their structures. As a result of our experiments we have succeeded in establishing the optimum conditions for the dehydrogenation of isopentane and in finding an alumina-chromia catalyst promoted by potassium oxide (90.7 mole-% Al_2O_3, 5.6 mole-% Cr_2O_3, 3.7 mole-% K_2O) in presence of which a catalyzate containing 38% of isopentenes (33% on the amount of original isopentane) is formed.

EXPERIMENTAL

The dehydrogenation reaction was carried out under atmospheric pressure at 527°. The catalysis tube contained 25 ml (17.5 g) of catalyst. Isopentane (b.p. 27.8-28.3°; n_D^{20} 1.3540; d_4^{20} 0.6200) was supplied in 10-ml portions from a spray buret at a space velocity of 0.5 hour^{-1}. After the fourth portion had been passed (40 ml), the catalyst was regenerated by treatment with air for 2 hours at 550°. The catalyst could be used in the reaction for 160 hours without appreciable loss of activity. A combined catalyzate obtained in experiments carried out under these conditions boiled over the range 20.0-148.0° (corrected) and had the following properties: n_D^{20} 1.3690, d_4^{20} 0.6340; iodine number 137.8; content of unsaturated hydrocarbons 37.9%. It was obtained in 87.0% yield. Analysis of the gas: hydrogen 85.2%; paraffin hydrocarbons 13.8%; unsaturated hydrocarbons 1.0%. The catalyzate (174.3 g) was fractionated through a 40-plate column. The results of the fractionation and the properties of the fractions are given in the table.

Investigation of Catalyzate Fractions. Fraction I. This contains isopentane and 3-methyl-1-butene. This is confirmed not only by the properties of the fraction, but also by Raman spectrum investigation. The value of the iodine number indicates that the 3-methyl-1-butene content is 13.2% (1.5% on the whole catalyzate).

Fraction II. Apart from unchanged isopentane, this contains approximately equal amounts (as determined from the Raman spectrum) of 3-methyl-1-butene and 2-methyl-1-butene. The value of the iodine number indicates that the total content of unsaturated hydrocarbons in this fraction is 10.8% (about 5.4% of each of the isopentenes, or 2.9% of each on the whole catalyzate).

Fraction III. Aanlysis by the Raman spectrum method indicates that this fraction contains isopentane, 2-methyl-1-butene, 2-methyl-2-butene, and probably 1-pentene. 2-Methyl-2-butene predominates among the unsaturated hydrocarbons. The total content of unsaturated hydrocarbons in the fraction is 40% (1.4% on the whole catalyzate).

Fraction IV. The value of the iodine number indicates that this fraction contains 82.6% of unsaturated hydrocarbons (24.6% on the whole catalyzate), which probably consist mainly of 2-methyl-2-butene. It is possible that it contains very small amounts of 2-methyl-1-butene. The saturated part of the fraction was not investigated, but the boiling range indicates that it consists mainly of n-pentane.

Fraction V. This fraction, and also Fraction VI, was isolated by fractionation from a small flask fitted with a column. It contains 61.1% of unsaturated hydrocarbons (1.7% on the whole catalyzate), mainly 2-methyl-2-butene, but also a little cis-2-pentene (determined by the Raman spectrum method).

Fraction VI. Most of this fraction came over at 110°. Its infrared absorption spectrum was determined, and it indicated that the fraction consists mainly of toluene; a little 2-methyl-2-butene (0.6% on the fraction) is also present. These results are confirmed by the properties of the fraction.

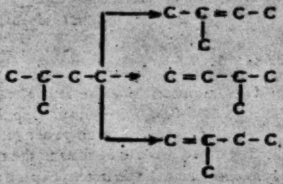
Hence, in the dehydrogenation of isopentane in presence of an alumina-chromia catalyst promoted by potassium oxide, a mixture of isopentenes is obtained. It consists mainly of 2-methyl-2-butene, and contains also the other two possible isopentenes – 3-methyl-1-butene and 2-methyl-1-butene. Other substances found in the catalyzate in small quantities are 1-pentene, 2-pentene, toluene, and, apparently, n-pentane. On the basis of our results we consider that

TABLE

Properties of Fractions of Combined Isopantane Catalyzates

Fraction No.	Boiling limits in °C (corrected)	Amount (%)	n_D^{20}	d_4^{20}	Iodine number	Content of unsaturated hydrocarbons (% by weight)
I	20.0-25.0	11.7	1.3560	0.6223	48.0	13.2
II	25.0-30.0	50.9	1.3580	0.6230	39.2	10.8
III	30.0-36.0	3.5	1.3775	0.6485	145.0	40.0
IV	36.0-39.0	28.8	1.3815	0.6530	300.0	82.6
V	39.0-43.5	2.8	1.3990	0.6728	221.3	81.5
VI	43.5-148.0	1.8	1.4850	0.8426	2.2	0.6
Residue	–	0.1	1.5110	–	–	–

the main reactions of 2-methylbutane under the conditions of our experiments are:



As regards the formation of aromatic hydrocarbons, this is a matter for further investigation.

SUMMARY

A catalyst was found for the dehydrogenation of isopentane to isopentenes, namely, a mixture of the oxides of chromium, aluminum, and potassium. The optimum conditions for its action were determined.

LITERATURE CITED

[1] E. A. Timofeeva, S. S. Novikov, and N. I. Shuikin, Proc. Acad. Sci. USSR, 92, No. 2, 345 (1953).

[2] N. I. Shuikin, E. A. Timofeeva, and V. M. Sladkikh, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, No. 3, 567, (T.p. 503)*.

Received June 7, 1955

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

---

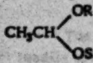
* T.p. = C. B. Translation pagination

SYNTHESIS AND REACTIONS OF OXYGEN-CONTAINING ORGANOSILICON COMPOUNDS

COMMUNICATION 2. REACTIONS OF DIETHYL- AND DIPHENYL-SILANEDIOLS WITH VINYL ETHERS

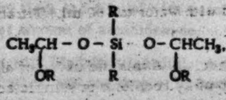
M. F. Shostakovsky, D. A. Kochkin, and V. M. Rog

This paper describes the further investigation of organosilicon compounds containing hydroxyl groups. It was shown previously that trialkyl- or triaryl-silanols R_3SiOH react with alkyl vinyl ethers with formation of organosilicon acetals



$CH_3CH(OR)(OSiR_3)$

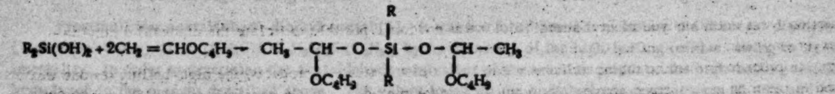
[1-3]. In the present investigation we have studied the reactions of dialkyl- and diaryl-silanediols (the examples taken being diethyl- and diphenyl-silanediols) with vinyl ethers with the object of preparing organosilicon diacetals:



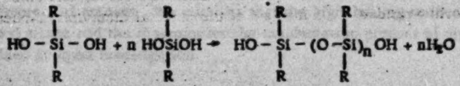
$$CH_3CH(OR)-O-SiR_2-O-CH(OR)CH_3,$$

(R is alkyl or aryl)

No acetals of such structure have been described in the literature. Reaction between butyl vinyl ether and diethyl- and diphenyl-silanediols proceeds with the formation of several by-products, as indicated by the following equations:



$$R_2Si(OH)_2 + 2CH_2=CHOC_4H_9 \rightarrow CH_3-CH(OC_4H_9)-O-SiR_2-O-CH(OC_4H_9)-CH_3 \quad (1)$$



$$HO-SiR_2-OH + n\,HOSiR_2OH \rightarrow HO-SiR_2-(O-SiR_2)_nOH + nH_2O \quad (2)$$

$$CH_2=CHOR + HOH \xrightarrow{HCl} ROH + CH_3CHO \quad (3)$$

$$CH_2=CHOR + ROH \rightarrow CH_3CH(OR)_2 \quad (4)$$

Apart from organosilicon diacetals, the products isolated included acetaldehyde dibutyl acetal and alkyl- or aryl-substituted polysiloxanes, which confirms the reaction scheme given above. The optimum conditions for the formation of organosilicon diacetals were found to be as follows: considerable excess of the vinyl ether, use of acids as catalysts, and heating of the reaction mixture for 90-120 minutes 60°. The reaction is then displaced in the direction of preferential formation of diacetal (Equation 1), and the accompanying reactions (Equations 2-4) are largely suppressed. The structure of the diacetal obtained from diethylsilanediol was confirmed by hydrolysis with 5% sulfuric acid, which proceeds according to the following equation:

$$[CH_3CH(OC_4H_9)O]_2Si(C_2H_5)_2 + 2HOH \xrightarrow{H^{+}} 2CH_3CHO + 2C_4H_9OH + (C_2H_5)_2Si(OH)_2.$$

EXPERIMENTAL *

Preparation of the Diacetal Bis (1-butoxyethoxy)diethylsilane. A mixture of 12.0 g of diethylsilanediol (m.p. 92.0-92.5°)** 50 g of butyl vinyl ether (b.p. 93.0-94.0°; n_D^{20} 1.4018; d_4^{20} 0.7792), and one drop of concentrated hydrochloric acid was prepared in a sealed tube, which was heated for 90-120 minutes at 60° and then set aside overnight. The mixture was neutralized with potassium carbonate and fractionated, the following fractions being collected:

Fraction I, B.p. 60-68° (12 mm); n_D^{20} 1.4100; d_4^{20} 0.8273; 4.2 g
Fraction II, B.p. 126-133° (6 mm); n_D^{20} 1.4260; 11.5 g
Fraction III, high-boiling products.

Butyl vinyl ether was collected in a trap. Fraction I was acetaldehyde dibutyl acetal [5]. Refractionation of Fraction II yielded 10 g (37%) of the diacetal bis (1-butoxyethoxy) diethylsilane, b.p. 127-129° (5 mm); n_D^{20} 1.4270; d_4^{20} 0.9010; found MR 91.49; calculated for $C_{16}H_{34}SiO_4$ MR 90.90; found M (in benzene) 303.5; 310.0; calculated M 320.5.

Found %: C 60.56; 60.63; H 11.42; 11.34; Si 8.36, 8.44
$C_{16}H_{34}SiO_4$. Calculated %: C 60.00; H 11.32; Si 8.75

The high-boiling product was found to be polydiethylsiloxane. The acetal is a clear liquid of ethereal odor, readily soluble in ether and alcohol.

Hydrolysis of Bis (1-butoxyethoxy)diethylsilane. The diacetal (0.5 g) was heated with 50 ml of 5% sulfuric acid in a sealed tube in a boiling water bath until a homogeneous solution was obtained (3-4 hours). The contents of the tube were transferred to a measuring flask and diluted with water to 200 ml. Titration by the bisulfite method gave 94.99% and 96.3% of the theoretical amount of acetaldehyde.

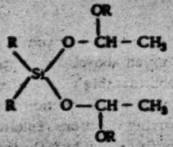
Reaction of Butyl Vinyl Ether with Diphenylsilanediol. A mixture of 5 g of diphenylsilanediol (m.p. 139°)***, 50 g of butyl vinyl ether, 20 ml of ether, and one drop of hydrochloric or sulfuric acid was prepared in a sealed tube, which was heated in a boiling water bath until the diphenylsilanediol dissolved completely (a few hours). The mixture was neutralized and fractionated, the following products being obtained:

Fraction I, B.p. 55° (1.5 mm); n_D^{20} 1.4089; d_4^{20} 0.8259; 2.5 g
Fraction II, high-boiling residue

Fraction I was acetaldehyde dibutyl acetal [5]. It was not found possible to isolate the diacetal diethylbis-(1-phenoxyethoxy) silane $(CH_3CHOC_4H_9O)_2Si(C_6H_5)_2$ by fractionation of the high-boiling residue, owing to its thermal instability. In order to determine the acetaldehyde equivalent of the reaction products, the high-boiling residue was hydrolyzed in the manner described above. The values found for the acetaldehyde content were 83.46% and 82.83% of the theoretical amount. We consider that the high-boiling residue was a mixture of the diacetal diethylbis (1-phenoxyethoxy) silane and the macromolecular condensation product of diphenylsilanediol. The nature of the compounds obtained is under investigation.

SUMMARY

1. The reactions of diethyl- and diphenyl-silanediols with butyl vinyl ether were investigated. It was shown that oxygen-containing organosilicon compounds could be obtained, namely diacetals of general structure:



---

* Junior scientific worker A. M. Gutman participated in the work.

** Diethylsilanediol was prepared by the hydrolysis of dichlorodiethylsilane with N NaOH, and the dichlorodiethylsilane was prepared by direct synthesis from ethyl chloride [4].

*** Prepared by the hydrolysis of dichlorodiphenylsilane with N NaOH or N KOH. It was found that diphenylsilanediol was best crystallized from a mixture of ether and isopentane.

2. These diacetals were obtained only when an excess of the vinyl ether was used.

LITERATURE CITED

[1] M. F. Shostakovsky, I. A. Shikhiev, and D. A. Kochkin, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, No. 5, 941 (T.p. 837)*.

[2] M. F. Shostakovsky, K. A. Andrianov, I. A. Shikhiev, and D. A. Kochkin, Proc. Acad. Sci. USSR, 93, 641 (1953).

[3] M. F. Shostakovsky and D. A. Kochkin, Proc. Acad. Sci. USSR, 95, No. 4, 821 (1954).

[4] K. A. Andrianov and D. A. Kochkin, Authors' Certif. No. 71050 (1947); Authors' Certif. No. 9517 (1949); Bulletin of Inventions No. 4, 16 (1948).

[5] M. F. Shostakovsky and N. A. Gershtein, J. Gen. Chem., 16,7, 946 (1946).

OBITUARY

ALEKSANDR VASILYEVICH TROFIMOV

Aleksandr Vasilyevich Trofimov, senior scientific worker and one of the foremost members of the staff of the Vernadsky Institute of Geological and Analytical Chemistry of the USSR Academy of Sciences, died suddenly at Vilyuisk at 8 a. m. on June 19, 1955, while out on an expedition.

A. V. Trofimov was born in Moscow in 1899. In 1923, while still a student and before completion of his course at the Timiryazev Agricultural Academy, Trofimov began an investigation of the chemistry and physical chemistry of soils in the General Agriculture Department. During this period and the period following graduation (up to 1930), he worked as a chemist in the Timiryazev Agricultural Academy and published a series of papers on moisture relations and structure in soils; he studied the penetration of water into soils, the reaction of soils as a function of moisture, and acid exchange in solutions in contact with soils.

In 1930 Trofimov took up work at the State Oceanography Institute (reorganized later as a part of the All-Union Fishery and Oceanography Research Institute- VNIRO), where he studied the physical chemistry of the sea: chemical composition of sea water, submarine actinometry, and iodiferous seaweeds. These investigations are still extensively cited, not only here, but also abroad.

Later, Trofimov obtained some very valuable experience in precision instrument-making at the Moscow Experimental Station for the Construction of Control and Measuring Instruments and also, subsequently at the Air Force Research Institute. He showed himself to have the qualities of a first-class instrument maker, and he became well-versed in the intricacies of this complicated work.

After demobilization in 1944 from the Red Army, Trofimov took up a post as senior scientific worker at the Vernadsky Institute of Geological and Analytical Chemistry of the USSR Academy of Sciences. Since then Trofimov's scientific activities have been wholly associated with a new field of knowledge – the geochemistry of isotopes. His investigations took up three main directions: the geochemistry of stable isotopes of carbon, sulfur, oxygen, and argon; the determination of the absolute geological age of recent formations by the carbon method; and investigations on meteorites by the isotope method. In order to carry out these investigations, Trofimov designed unique apparatus (mass-spectrometers and counters for the determination of C-14). As a result of his investigations Trofimov made some important geochemical generalizations. On the basis of the identity in mean isotopic composition of the carbon of the primary igneous rocks of the earth and the carbon of meteorites, he confirmed experimentally the hypothesis of the genetic identity of the substance of the earth and that of meteorites. The same conclusion was confirmed by investigation of the isotopic composition of sulfur from meteorites and from the earth's crust. He provided experimental confirmation of V. I. Vernadsky's hypothesis of the preponderance of organic carbon over carbonate carbon in the earth's crust.

Trofimov's investigations on the isotope exchange of the oxygen of carbonate indicated the great stability of these deposits in geological time. This conclusion is very important for the paleothermometric method, which is now used in climatology and geology.

Trofimov worked on the determination of the absolute geological age of sedimentary formations with the aid of C-14; in particular, he worked on the sedimentary rocks of the Yakutsk Republic. He determined the geological ages of the soils of the Taimyr peninsular and the time of the existence of the Taimyr mammoth.

The premature death of A. V. Trofimov came at the very height of his creative work. He was a true Soviet scientist – his life devoted entirely to science. In his person there was a happy combination of the brilliant experimentalist and the creator of broad generalizations.

He was well-versed in the most varied fields of science, and at the same time he had a very original turn of mind. He was a highly talented investigator. Trofimov was a very loyal colleague, who will never be forgotten by those who met him. He freely shared his knowledge with others and he made great demands on himself. He shone out as an example of an indefatigable worker, a highly conscientious man, distinguished by a rare modesty.

The death of Aleksandr Vasilyevich Trofimov is a grievous loss to science, and it brings the deepest sorrow to all his colleagues and friends.

Vernadsky Institute of Geological and Analytical Chemistry of the USSR Academy of Sciences

SALUTATION TO ALEKSANDR NAUMOVICH FRUMKIN

on the Occasion of his Sixtieth Birthday

The Division of Chemical Sciences of the Academy of Sciences of the USSR and the Editorial Board of the Bulletin of the Academy of Sciences, Division of Chemical Sciences congratulate you on the occasion of your sixtieth birthday and of the completion of forty years of scientific activity.

Your many and varied physicochemical investigations— particularly in the field of electrochemistry —form a very significant contribution to science.

We hope that you will enjoy good health and will continue in your successful creative work.

DIVISION OF CHEMICAL SCIENCES OF THE ACADEMY OF SCIENCES OF THE U S S R.

EDITORIAL BOARD OF THE BULLETIN OF THE ACADEMY OF SCIENCES OF THE U S S R,
DIVISION OF CHEMICAL SCIENCES

EFFECT OF THE METHOD OF MAKING MODIFYING ADDITIONS ON THE PROPERTIES OF OXIDE CATALYSTS

G. M. Zhabrova and E. A. Fokina

The way in which additives are distributed at the surface and in the body of a catalyst and the possibility of interaction between additives and the catalyst are matters of great interest for the understanding of the laws governing the action of additives on catalysts. It was considered probable that change in the method of introducing additives can result in a change in their distribution in the catalyst and have a substantial effect on the catalytic properties of the catalyst.

As a model reaction of the oxidation-reduction type we made use of the decomposition of hydrogen peroxide in presence of magnesium oxide [1]. It was found that, in the pure state, magnesium oxide has only moderate catalytic activity, and this facilitated the detection of positive effects attributable to additions. Stannic oxide was selected as additive; in the pure state this substance has a negligible catalytic effect. The rate of decomposition of hydrogen peroxide was determined gasometrically, the procedure being similar to that described previously [1].

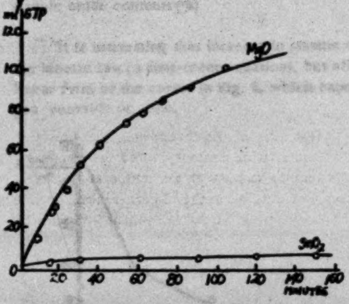


Fig. 1. Kinetic curves for the decomposition of hydrogen peroxide over magnesium oxide and over stannic oxide (reaction temperature 45°)

Fig. 1 shows kinetic curves for the decomposition of hydrogen peroxide over pure magnesium oxide and over pure stannic oxide. It will be seen that the activity of the former is about 35-40 times as great as that of the latter. As stannic oxide is introduced into the magnesium oxide in small amounts (0.01-6.4%), the effect of the simple summation of the activities of the two oxides can be neglected.

For the introduction of stannic oxide into magnesium oxide, the following three methods were used:

1. Impregnation of prepared magnesium oxide with solutions of tetraphenyltin. Magnesium oxide is impregnated with chloroform solutions of tetraphenyltin at various concentrations, dried at 100-120°, and calcined for one hour at 600° in a quartz vessel in an atmosphere of air. Pyrolysis of tetraphenyltin gives phenyl radicals and atomic tin, which is oxidized by atmospheric oxygen to stannic oxide (Series 1).

2. Impregnation of prepared magnesium oxide with solutions of stannic chloride. Magnesium oxide is impregnated with aqueous stannic chloride solutions of various concentrations, and the stoichiometric amount of 20% sodium carbonate solution is added to the resulting paste. The catalyst samples prepared in this way are washed, dried, and calcined for four hours at 450° in a quartz vessel in an atmosphere of air (Series 2).

3. Coprecipitation of magnesium and tin salts with sodium carbonate solution, the basic carbonates formed being washed, dried, and calcined at 450° (Series 3).

The amount of stannic oxide introduced was determined by polarography and spectrum analysis.

For our study of the catalytic properties of the magnesium oxide samples containing additions of stannic oxide it was necessary to select a method of determining the relative activities of the samples. It was established that the course of the decomposition of hydrogen peroxide is satisfactorily described by a first-order equation. The value of the rate constant served as a measure of the activity of the catalyst. Rate constants could be determined accurate within 5%.

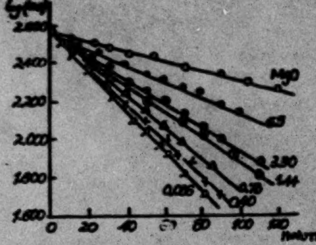


Fig. 2. Kinetic curves for the decomposition of hydrogen peroxide plotted in accordance with the first-order law for the samples of Series 1. The decomposition reaction was carried out at 90°. The figures on the curves denote stannic oxide contents (%)

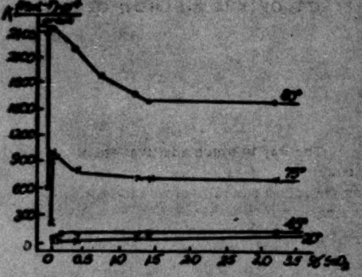


Fig. 3a. Dependence of the activity of catalyst samples of Series 1 on stannic oxide content. The figures on the curves denote reaction tempertures

It is interesting that increase in stannic oxide content form 0.048 to 6.3% by weight did not alter the form of the kinetic law (a first-order equation), but affected only the value of the rate constant. This can be seen from the linear form of the curves in Fig. 2, which express the dependence of the logarithm of the amount of unchanged hydrogen peroxide on time.

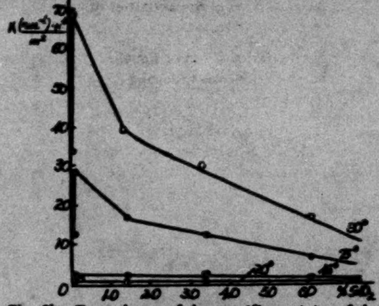


Fig. 3b. Dependence of the specific activity of the same samples on stannic oxide content.

Our study of the dependence of catalyst activity on stannic oxide content showed that the form of this relationship varies with the temperature of the reaction. This is illustrated in Fig. 3a for reaction temperatures ranging from 20° to 90°. Thus, at 90° there is a maximum at an additive content of 0.086%, and at this point the activity is 4.1 times as great as that of pure magnesium oxide. At 75° there is a maximum at the same stannic oxide content, but the effect of the addition is somewhat less than at 90°.

When the reaction temperature is lowered further to 45°, the maximum moves from 0.086% to 0.40%, and the activity relative to that of pure magnesium oxide is 2.1. Finally, at still lower temperatures (20° and 5°), the maximum disappears, and, beginning from the very smallest amounts of additive, the activity is less than that of pure magnesium oxide. As the temperature of the catalytic reaction is lowered, the curves for the dependence of the specific activity of the catalyst on additive content flatten out (Fig. 3b).

This behavior indicates that the value of the activation energy varies for the different catalyst samples (pure magnesium oxide and magnesium oxide containing stannic oxide). A summary of data on the activation energy and pre-exponential factor is given in Table 1. The probable error in the determination of activation energy is ±0.5 kcal / mole.

It follows from the data in Table 1 that a substantial change in the activation energy and in the logarithm of the pre-exponential factor is brought about by the first very small additions of stannic oxide. In the further range of additions from 0.40 to 3.30, the variations in activation energy and in the logarithm of the pre-exponential factor are approximately equal to the experimental error. At high stannic oxide contents both quantities are reduced somewhat.

TABLE 1

Dependence of the Activation Energy and the Logarithm of the Pre-exponential Factor on the Stannic Oxide Content of a Magnesium Oxide Catalyst (Series 1)

SnO_2 content (%)	E (kcal/mole)	log K_0
None	13.0	6.6
0.046	17.5	9.7
0.086	18.0	10.2
0.095	17.5	9.7
0.40	17.5	9.6
0.78	17.0	9.5
1.20	17.5	9.6
1.44	17.0	9.4
3.30	17.0	9.4
6.30	16.5	9.0

The values of the pre-exponential factor vary symbatically with the values of the activation energy. It should be noted that a symbatic relationship between E and log K_0 as the content of additives in oxide catalysts is increased was observed by Todes and Margolis [2] and by Margolis and Krylov [3] for the high-temperature oxidation of isooctane. The more marked dependence of catalyst activity on stannic oxide content at higher temperatures gives reason to suppose that stannic oxide is a modifying additive [4, 5].

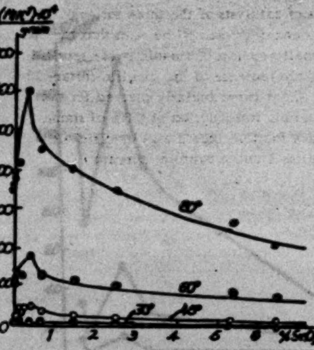


Fig. 4a. Dependence of the activity of catalyst samples of Series 2 on stannic oxide content (at various reaction temperatures).

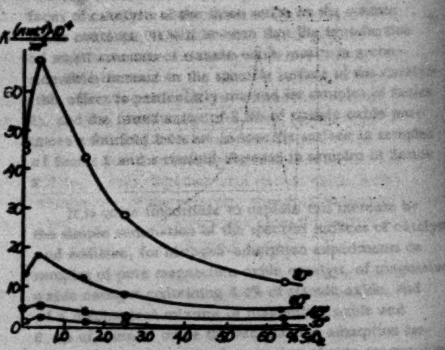


Fig. 4b. Dependence of the specific activity of the same samples on stannic oxide content

Similar regularities, though not so marked, are to be observed for the preparations of Series 2. For the maximum point (0.4% SnO_2) at 80°, the activity of the modified catalyst is 1.7 times as great as that of pure magnesium oxide. As the temperature is lowered, this ratio diminishes (Fig. 4a). As in the previous case, the observed variation in the form of the curve for catalytic activity against additive content is to be attributed to the variation in the values of the activation energy and pre-exponential factor for reactions over the catalyst samples (pure magnesium oxide and magnesium oxide with various additions of stannic oxide). The range of variation is somewhat less here than in Series 1: the activation energy varies from 14.0 to 16.5 kcal/mole, and the logarithm of the pre-exponential factor from 7.7 to 9.8. Hence, similar regularities are found both when the introduction of stannic oxide into prepared magnesium oxide is made originally in the form of an organic tin compound, and when it is intorduced as an inorganic tin compound.

The behavior found when the catalyst is prepared by the coprecipitation of magnesium and tin salts (Series 3) differs greatly from that found in Series 1 and 2, in which the additive was formed on the prepared catalyst, the curve for catalytic activity against additive content now having a minimum corresponding to a content of 0.02% SnO_2 and a maximum corresponding to 1.0% SnO_2 (Fig. 5). The increase in activity at the maximum point (as compared with the activity of the pure oxide) is only slight, the ratio of constants being 1.3 at 80°. It should be noted that the form of the curve for rate constant against content of modifying addition (Fig. 5) is similar to that of the curve for the rate constant of hydrogen peroxide decomposition at platinized platinum treated with a catalytic poison (arsenious oxide), as determined by Shlygin [6]. Element [7], who investigated the effect of additions of aluminum oxide and silicic acid to nickel oxide in oxidation reactions, also observed a complicated relationship between catalytic activity and additive content, there being a minimum and a maximum catalytic activity.

Returning now to the consideration of our results, we must point out that for this series of catalysts the activation energy and pre-exponential factor again vary within very narrow limits with variation in the amount of additive introduced. Thus, for pure magnesium oxide, and also for magnesium oxide containing 6% of stannic oxide, the activation energy is 14.0 kcal/mole, whereas for magnesium oxide containing 1% of stannic oxide – E = 16.0 kcal/ /mole.

In order to obtain a more accurate picture of the action of the modifying addition and the dependence of its effect on the method by which it is introduced, the study of the catalytic properties of the samples was supplemented by an examination of their adsorptive properties (form of the nitrogen and heptane adsorption isotherms, their specific surfaces, etc.). It was then shown [8] that the introduction of stannic oxide onto prepared magnesium oxide (Series 1 and 2) leads to a marked increase in specific surface, whereas introduction of the same additive into magnesium oxide by the coprecipitation method (Series 3) has almost no effect on the specific surface of the catalyst.

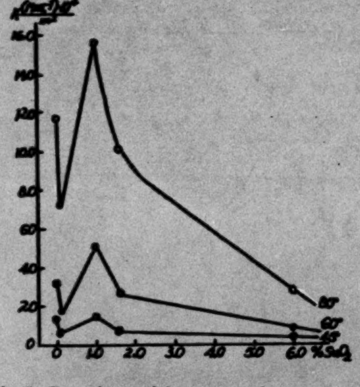


Fig. 5. Dependence of the activity of magnesium oxide catalysts of Series 3 on stannic oxide content (at various reaction temperatures)

Fig. 6 shows the dependence of the specific surfaces of catalysts of the three series on the stannic oxide contents. It will be seen that the introduction of small amounts of stannic oxide results in a considerable increase in the specific surface of the catalyst (this effect is particularly marked for samples of Series 1), and the introduction of 6.3% of stannic oxide produces a fourfold increase in specific surface in samples of Series 1 and a twofold increase in samples of Series 2.

It is quite impossible to explain this increase by the simple summation of the specific surfaces of catalyst and additive, for nitrogen-adsorption experiments on samples of pure magnesium oxide catalyst, of magnesium oxide catalyst containing 6.4% of stannic oxide, and of a mechanical mixture of magnesium oxide and 6.4% of stannic oxide showed that the adsorption isotherm of the mixture is close to that of pure magnesium oxide (Fig. 7). It may be noted also that, as indicated by an elementary calculation, for simple summation to be possible it must be assumed that the stannic oxide introduced has a physically unreal specific surface (more than 1000 sq.m/g). All these considerations, supported also by results from measurements of the pore structures of the catalysts, led us to the conclusion [8] that the introduction of stannic oxide by the impregnation of prepared magnesium oxide probably results in the formation of a surface compound of tin and magnesium oxides and the breaking-up of the magnesium oxide surface. On the other hand, the introduction of stannic oxide into magnesium oxide by the coprecipitation method results in the preferential distribution of the additive within the micrograins of the catalyst.

Fig. 8 represents the dependence of specific activity (expressed as the unimolecular rate constant for the decomposition of hydrogen peroxide divided by the specific surface of the catalyst) on the stannic oxide content of the magnesium oxide catalyst. The same figure shows also the dependence of the specific surface of the catalyst on the stannic oxide content, which is expressed by a curve that rises steeply at first and then passes over into a more gently rising portion. The region of the transition from the sharp rise to the gentle slope corresponds closely to the region of optimum catalytic activity on the modification curve. This behavior gives rise to the hypothesis of a change in the chemical composition of the catalyst surface in the region of optimum catalytic activity, probably associated with the formation of a special kind of surface compound between stannic oxide and magnesium oxide (possibly a type of stannate) which breaks up the magnesium oxide surface. It is evident that, as the stannic oxide content of the magnesium oxide catalyst is increased, separate patches of finely dispersed stannic oxide are formed on the surface, with the result that partial blocking of the surface occurs. This change in the catalyst surface corresponds to the gently sloping part of the curve for the change in specific surface, and it is accompanied by a fall in catalytic activity. It may be supposed that with further increase in the stannic oxide content a more complete blocking of the magnesium oxide surface occurs as a result of the formation of a layer of finely dispersed stannic oxide. As the catalytic activity of stannic oxide is very much less than that of magnesium oxide, this blocking must result in very much reduced catalytic activity in magnesium oxide samples having a high stannic oxide content, and our observations on a catalyst sample having a 20% stannic oxide content confirm this. It should be noted that only at stannic oxide contents of 3% and greater do the lines of stannic oxide appear in the X-ray diffraction pictures of the samples (Series 1 and 2).

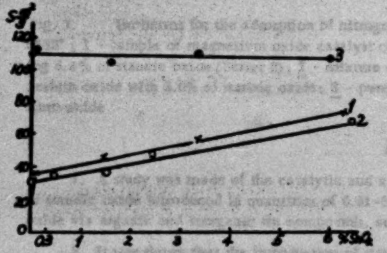


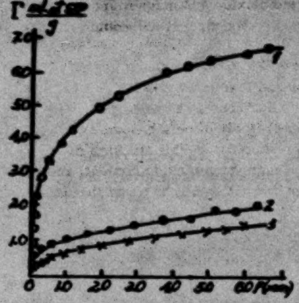
Fig. 6. Dependence of the specific surface of the catalyst (determined by the adsorption of heptane) on the content of stannic oxide introducted by different methods).

A different picture is observed when the addition of stannic oxide is made by the coprecipitation method. The lack of dependence of specific surface on stannic oxide content gives reason to suppose that the stannic oxide is mainly within the micrograins of the catalyst and only a very small portion of it is on the catalyst surface. Accordingly, the stannic oxide content at the maximum point (1%) is much greater than at the maxima of the modification curves of catalyst samples of Series 1 and 2 (0.086% and 0.4%). It is evident that, in the present case, no finely dispersed film of stannic oxide is formed on the catalyst surface at higher stannic oxide contents; X-ray diffraction pictures support this view, weak SnO_2 lines being found only in samples containing 6.0% or more of stannic oxide. It must be supposed that here again magnesium stannate is formed and occurs, together with stannic oxide, within the micrograins of the catalyst. However, it is clear that we are dealing with a complex case of modification which deserves more detailed study.

Our results enable us to infer that in the catalytic system investigated the method of introducing the additive has an important effect on the properties of the catalyst and on the way in which the additive acts. The method of introducing the additive by treatment of the prepared catalyst – which we effected by impregnation of magnesium oxide with organic and inorganic tin compounds and subsequent pyrolysis – apparently leads to the formation of surface compounds between the catalyst and the additive, to the breaking-up of the surface, and to the modification of the catalyst. Considered in relation to the classification of catalyst additives proposed by Roginsky [4], stannic oxide, introduced by this method, may be considered to be both a modifying and a structure-forming additive.

The coprecipitation method contrasts sharply with the above-mentioned methods and results in quite a different distribution of stannic oxide in the magnesium oxide (essentially within the micrograins of the catalyst). The way in which the additive acts is also quite different, the dependence of catalyst activity on stannic oxide content being represented by a complex curve having a maximum and a minimum.

In conclusion it must be pointed out that most investigators have assumed that the chemical composition of the catalyst and additive unequivocally determines the manner in which the catalytic system acts. From the data provided by the present investigation it will be clear that for a given additive content in the catalyst the action of the catalyst, and also, probably, the additive concentration at the catalyst surface, may vary greatly according to the method used for introducing the additive. It is probable that catalysis and adsorption effects attributable to the method of introducing additives are not limited to the particular system that we have studied, but constitute a factor that must be taken into account in other catalytic systems.



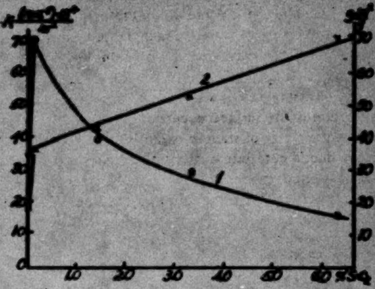


Fig. 7. Isotherms for the adsorption of nitrogen at −183° ; 1 - sample of magnesium oxide catalyst containing 6.4% of stannic oxide (Series 2); 2 - mixture of magnesium oxide with 6.0% of stannic oxide; 3 - pure magnesium oxide

Fig. 8. Dependence of the specific activity (1) and the specific surface (2) of magnesium oxide samples of Series 1 on stannic oxide content

SUMMARY

1. A study was made of the catalytic and adsorptive properties of magnesium oxide samples containing additions of stannic oxide introduced in quantities of 0.01-6.4% by various methods: by application to prepared magnesium oxide via organic and inorganic tin compounds, and by coprecipitation.

2. It was shown that the introduction of stannic oxide into magnesium oxide by impregnation with tetraphenyl tin or stannic chloride results in a modification of the action of the magnesium oxide catalyst in the decomposition of hydrogen peroxide. The main effect is already brought about [illegible] very smallest additions of stannic oxide. As the temperature of the catalytic process is lowered from 90° to 5°, the modification curves change in form, becoming flattened out.

3. The dependence on stannic oxide content of the activity of catalysts prepared by the coprecipitation of magnesium and tin salts is expressed by a curve having a minimum and a maximum. Minimum catalytic activity corresponds to a stannic oxide content of 0.02% and maximum activity to a stannic oxide content of 1%.

4. Change in the method of introducing the additive not only affects the catalytic properties, but also — as we showed previously — results in a marked change in the adsorptive properties of the catalyst. When stannic oxide is introduced into prepared magnesium oxide, the adsorptivity and specific surface of the sample increases with increase in additive content. When stannic oxide is introduced into magnesium oxide by coprecipitation, the adsorptivity and specific surface of the products are almost unaffected by increase in additive content.

5. On the basis of a comparison of the catalytic and adsorptive properties of the catalysts studied, we have advanced the hypothesis that the ways in which additions of stannic oxide are incorporated into magnesium oxide are of two different types and that the manner in which the additions act depends on the method by which they are introduced into the catalyst.

The authors express their thanks to S. Z. Roginsky for his constant interest in this work and to M. Ya. Kushnerev for carrying out the X-ray-structure measurements.

LITERATURE CITED

[1] G. M. Zhabrova, S. Z. Roginsky, and E. A. Fokina, J. Gen. Chem., 24, 10 (1954) (T.p. 7)*.

[2] O. M. Todes and L. Ya. Margolis, Bull. Acad. Sci., USSR, Div. Chem., Sci., 1947, No. 5, 443.

[3] L. Ya. Margolis and O. V. Krylov, J. Gen. Chem., 20, 1991 (1950) (T.p. 2063)*.

[4] S. Z. Roginsky, Proc. Acad. Sci., USSR, 87, 1013 (1952).

[5] G. M. Zhabrova, Prog. Chem., 20, 450 (1951).

[6] A. I. Shlygin, Doctorate Thesis, Inst. Phys. Chem., Acad. Sci., USSR, Kirov State Univ., Kazan, 1947.

[7] N. I. Element, Candidate's Thesis, Moscow Inst. Chem., Eng., 1948.

[8] G. M. Zhabrova, S. Z. Roginsky, and E. A. Fokina, J. Phys. Chem., 29, No. 3, 558 (1955).

Received April 9, 1955

Institute of Physical Chemistry
of the USSR Academy of Sciences

---

* T.p.= C. B. Translation pagination.

SOLID SOLUTIONS OF CALCIUM ALUMINOFERRITES

N. A. Toropov and A. I. Boikova

Solid solutions of calcium aluminoferrites are formed in the ternary system $CaO - Al_2O_3 - Fe_2O_3$ by mutual solution of $2CaO \cdot Fe_2O_3$ and $5CaO \cdot 3Al_2O_3$ (and probably a small amount of calcium oxide).

The first investigators of the system $CaO - Al_2O_3 - Fe_2O_3$, Hansen, Brownmiller, and Bogue [1], established the existence of only one ternary compound $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ in the region of high calcium oxide contents. Tetracalcium aluminoferrite has high refractive indices $N_g = 2.08_{(Na)}$ and $N_p = 1.96_{(Na)}$, and it is pleochroic in dark to light brown tones. $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ and compounds whose fields of stability border on that of the aluminoferrite in the ternary system, namely, $3CaO \cdot Al_2O_3$, $5CaO \cdot 3Al_2O_3$, CaO, are important components of clinker. It is obvious that the system as a whole, and especially those parts bordering on the field of calcium oxide, is of considerable interest for the study of the structure of cement clinker. Particular attention has been turned on the investigation of ferrites and aluminoferrites. This interest has been aroused under the following circumstances. Lea and Parker [2] and Guttman and Gille [3], in investigations on synthetic calcium aluminoferrites and on the aluminoferrites of industrial clinkers, obtained crystals of these substances having lower refractive indices than $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. This could result by the dissolution in the aluminoferrites of compounds of lower refractive index, i.e. aluminates. Another very important fact confirmed the correctness of this last supposition. Investigation of the clinkers by crystal optics indicated a noncorrespondence between the actually observed and calculated (on the basis of chemical analysis) amounts of calcium aluminates. The calculated amount of aluminates was always greater than the actual amount.

One of the first investigations on solid solutions of calcium aluminoferrites was that of Toropov, Merkov, and Shishakov [4] on the binary system $5CaO \cdot 3Al_2O_3 - 4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. The system was studied by crystal optics and by X-ray methods. The formation of solid solutions was confirmed by the continuous lowering of the refractive indices of the aluminoferrites. The authors established that the maximum amount of $5CaO \cdot 3Al_2O_3$, dissolved by $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ is 35% by weight. The formula of the calcium aluminoferrite consisting of 35% by weight of $5CaO \cdot 3Al_2O_3$ and 65% by weight of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ is $43CaO \cdot 16Al_2O_3 \cdot 7Fe_2O_3$. Whereas the ferric oxide content of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ is 32.8% by weight, that of this aluminoferrite is 21.7% by weight. Calcium aluminoferrite of this composition has refractive indices of $N_g = 1.93$, $N_p = 1.87$. The authors confirmed the existence of solid solutions by X-ray diffraction.

Almost simultaneously with this work indications of solid solutions between $5CaO \cdot 3Al_2O_3$ and $4CaO_3 \cdot Al_2O \cdot Fe_2O_3$ were obtained by McMurdie [5], who concluded that $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ can dissolve only 5% by weight of $5CaO \cdot 3Al_2O_3$. However, according to Jamauchi [6], a homogeneous solid solution of composition $6.2CaO \cdot 2.2Al_2O_3 \cdot Fe_2O_3$ (21.8% by weight of ferric oxide) can exist. Newman [7] determined heats of solution for a series of solid solutions of aluminoferrites, and he showed that they depend linearly on composition.

The results of Toropov, Merkov, and Shishakov [4] have been criticized on several occasions -- right up to 1946, infact, when Swayze [8] confirmed their correctness. According to Swayze's results, a continuous series of solid solutions extends as far as the composition $6CaO \cdot 2Al_2O_3 \cdot Fe_2O_3$ (22.8% by weight of ferric oxide), or $42CaO \cdot 14Al_2O_3 \cdot 7Fe_2O_3$. When this formula is compared with $43CaO \cdot 16Al_2O_3 \cdot 7Fe_2O_3$, the formula given by the authors of the 1937 work, no great discrepancy is to be found. Moreover, the latter formula is appreciably closer in composition to the aluminoferrite having the maximum content of aluminate in solid solution (the so-called limiting solid solution). Actually, according to Swayze the limiting solid solution contains 22.8% by weight of ferric oxide, and according to Toropov, Merkov, and Shishakov it contains 21.7% by weight.

Hence, the composition proposed by Swayze for the final member of the series of solid solutions is only a rough approximation to the limiting composition of solid solutions. This is still more obvious when we consider the work of Italian investigators. Thus, Malquori [9] and Cirilli and Burdese [10], in X-ray studies of solid solutions of aluminoferrites, concluded that a homogeneous solid solution can be obtained having a ferric oxide content of 20-21%. Malquori [9] suggested that the formula of the aluminoferrite of maximum aluminate content is $6CaO \cdot 2.1Al_2O_3 \cdot 0.9Fe_2O_3$ (20.7% by weight of ferric oxide).

The originality of the procedure used by Cirilli and Brisi [11] for the investigation of aluminoferrites is worthy of note. They made use of the magnetic properties of aluminoferrites and measured their magnetic susceptibilities. They showed that the magnetic susceptibility of these substances increases as the alumina modulus increases and assumes a certain constant value from the point at which the molar ratio Al_2O_3/Fe_2O_3 attains the value of two. There is an inflection in the curve at the composition $6CaO \cdot 2Al_2O_3 \cdot Fe_2O_3$. As regards the accuracy of this method, we do not consider it very high, inasmuch as the inflection occurs at a point at which the aluminoferrite contains 22.8% by weight of ferric oxide. The results that we have discussed indicate that the limiting composition of the solid solutions corresponds to less than this content of ferric oxide, so that the inflection should occur to the left of the composition of 22.8% by weight of ferric oxide. However, the procedure described is of interest in that it permits the composition of aluminoferrites to be determined approximately from their magnetic characteristics.

Summarizing the results of the investigations examined, we may make the following statements. Between calcium ferrites and aluminates a series of solid solutions aluminoferrites is formed. In general, these solutions are formed by the partial replacement of iron by aluminum in dicalcium ferrite. Complete replacement would lead to dicalcium aluminate $2CaO \cdot Al_2O_3$, which does not exist as an individual chemical compound. Another aluminate — $5CaO \cdot 3Al_2O_3$ — appears on the phase diagram, and we consider that this substance forms solid solutions with calcium ferrite and a certain amount of calcium oxide. The compositions $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ and $6CaO \cdot 2Al_2O_3 \cdot Fe_2O_3$ should be regarded as intermediate members of this series of solid solutions.

EXPERIMENTAL

Selection of Method of Investigation. In view of the interest presented by this question, we set ourselves the tasks 1) of investigating solid solutions of aluminoferrites with the object of determining the composition corresponding to maximum saturation with aluminate; and 2) of determining whether aluminoferrites of variable composition are present in industrial clinkers.

We consider that, of all the above-mentioned methods for the investigation of solid solutions of aluminoferrites, the most accurate for these particular compositions is the method of crystal optics. It must be stated that few of the investigators of aluminoferrites have used this method. The sensitivity of one of the most accurate methods of investigation — the X-ray method — is low in the case of the aluminates and aluminoferrites with which we are concerned, and the contents of these in a mixture cannot be determined for less than the following values; $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ — 15%, and aluminates ($5CaO \cdot 3Al_2O_3$ and $3CaO.Al_2O_3$)— 6% [12]. On the other hand, when the optical method of investigation is used, these minerals can undoubtedly be determined in such amounts or even in very much less amounts (1-2%), when the large differences in refractive index are taken into account. In studying solid solutions of aluminoferrites by the X-ray method, Malquori, Cirilli, and Burdese did not take these important facts into account. Apart from the selection of the method of investigation, it was necessary also for us to arrange the conditions of the experiment so that the melts could be cooled as slowly as possible; in this way favorable conditions can be created for the crystallization of aluminoferrites when determining the composition of the solid solution having the maximum aluminate content. We shall not discuss the experimental arrangement for the synthesis; the melts were cooled at the rate of 1.5° per minute.

α'-$5CaO \cdot 3Al_2O_3$ as a Component of the Solid Solution. In order the resolve the question of the modification of aluminate that dissolves in the ferrite and the maximum content of aluminate in solid solution, a study was made of a series of compositions along the line of solid solutions which starts from dicalcium ferrite. As regards the section $2CaO \cdot Fe_2O_3 - 4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, Hansen, Brownmiller, and Bogue [1] have already established that a continuous series of solid solutions is formed between the components. This was later confirmed by the X-ray investigations of Solacolu [13].

We consider that the aluminate component of solid solutions of aluminoferrites is not the hypothetical $2CaO \cdot Al_2O_3$, as some investigators suppose, but $5CaO \cdot 3Al_2O_3$.

Pentacalcium trialuminate exists in two modifications: α-$5CaO \cdot 3Al_2O_3$, (cubic syngony; N = 1.608) and α'-$5CaO \cdot 3Al_2O_3$, (rhombic syngony; $N_g = 1.692$, and $N_p = 1.687$.

The rhombic modification of $5CaO \cdot 3Al_2O_3$, which is known as "unstable $5CaO \cdot 3Al_2O_3$", has the space group $P_{2_1 2_1 2}$ or P_{mmm} [14].

A study of rotation X-ray diagrams and Weissenberg diagrams of monocrystals of $2CaO \cdot Fe_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ enabled us to establish the space group $V_h^{28}(I_{mma})$ for the compounds. $2CaO \cdot Fe_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ belong to the rhombic syngony. The space group of pentacalcium trialuminate P_{mmm} (or $P_{2_1 2_1 2}$ and the space group of dicalcium ferrite and of tetracalcium aluminoferrite I_{mma} belong to the rhombic syngony.

It was natural to suppose that the solid solution of aluminoferrites was formed with the participation not of the cubic form of $5CaO \cdot 3Al_2O_3$, as previously considered, but of the rhombic modification, which is structurally closer to $2CaO \cdot Fe_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. In order to verify this supposition, we calculated the theoretical curve (Table 1) and constructed graphs for the dependence of the refractive index of the aluminoferrite on the ammount of α- or α'-$5CaO \cdot 3Al_2O_3$ dissolved in it. In this calculation we assumed additivity, i.e. a linear relation between the composition of the solid solutions and refractive index. A relation of this kind is closely followed in many systems containing solid solutions. By way of example we may cite the series investigated by Bowen and Schairer [15]: Mg_2SiO_4–Fe_2SiO_4, MgO–FeO, $MgSiO_3$–$FeSiO_3$.

We then synthesized solid solutions for the field of compositions in which the preparations consist of a single phase – a solid solution containing not less than 20% of ferric oxide. The refractive indices of these solid solutions were measured, and the values were plotted on the same diagram. It was found that the experimental values of the refractive index correspond to the values calculated for α'-$5CaO \cdot 3Al_2O_3$ of rhombic syngony (figure). In the further work we calculated the compositions of aluminoferrites on the assumption that the solid solution was formed with participation of the rhombic modification of $5CaO \cdot 3Al_2O_3$.

For the immersion investigation of aluminoferrites we used phosphorus immersion liquids obtained from the Geological Institute of the USSR Academy of Sciences. These liquids contained methylene iodide, white phosphorus, and sulfur. The refractive indices were measured in sodium light.

Limiting Concentration of the Solid Solution. By the term "limited concentration of the solid solution" is to be understood, in this case, the pentacalcium trialuminate concentration in the aluminoferrite solid solution having a maximum content of this substance. In order to resolve the main question – what is the maximum content of $5CaO \cdot 3Al_2O_3$ in the solid solution and to what limit the amount of ferric oxide is accordingly reduced in the limiting aluminoferrite? – we synthesized and studied mixtures containing 42, 32, 24, 20, 16, 14 and 12% by weight of ferric oxide. Table 2 shows the compositions of these mixtures.

Each sample was given four heat treatments: two sinterings and two fusions. The melts were cooled at 1.5° per minute. The samples were studied under the microscope by reflected and transmitted light. Samples containing more than 20% of ferric oxide consisted of homogeneous phases – solid solutions of aluminoferrites. Their grains showed pleochroism in light to dark brown tones. With increase in ferric oxide content the aluminoferrites became more and more intensely colored. Samples containing 16, 14, and 12% by weight of ferric oxide presented a different picture. In addition to aluminoferrite they contained also aluminates ($3CaO \cdot Al_2O_3$ and $5CaO \cdot 3Al_2O_3$), which are readily distinguished by reflected light (particularly after etching of the section with alcoholic oxalic acid) and when immersed. As the ferric oxide content of the samples increased from 14%, the refractive indices of the aluminoferrites present increased, but the aluminoferrites in the samples containing 14 and 12% of ferric oxide had identical refractive indices. This gave us reason to suppose that in these two samples the compositions of the aluminoferrites were identical. We therefore considered that the limiting composition of the solid solution (having the maximum aluminate content) had been reached.

Hence, the maximum lowering of the refractive index of the aluminoferrites is observed in samples containing 14 and 12% of ferric oxide. From the values Ng = 2.08 and Np = 1.98 for $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ we derived the values of Ng = 1.914 and Np = 1 854 (birefringence – 0.06) for the sample having the maximum content of aluminate in solid solution (limiting solid solution). The compositions of the aluminoferrites were calculated from these data.

Table 3 gives the results of the optical investigation of the synthetic aluminoferrites, their compositions expressed in weight and mole percentages, and their formulas. The composition of the aluminoferrite having the maximum content of pentacalcium trialuminate in solid solution is expressed by the formula $7.8CaC \cdot 3.24Al_2O_3 \cdot 1Fe_2O_3$. The limiting composition of the solid solution can be presented approximately in the form $8CaO \cdot 3Al_2O_3 \cdot Fe_2O_3$ (17.5% by weight of ferric oxide). The amount of ferric oxide is 17.2% by weight.

Structure of Aluminoferrites. A very general idea of the structure of aluminoferrites can be gained from the structure of tetracalcium aluminoferrite, which was partially investigated by Büssem [16]. The elementary cell contains two $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ molecules and has the parameters a_0 = 5.34 A, b_0 = 14.14 A, c_0 = 5.52 A.

According to Büssem, the rhombic lattice must consist of layers of FeO_4 tetrahedra united in one direction and attached by oxygen bridges to layers of AlO_6 octahedra at a distance of $^1/_4$b. Ca ions are arranged between the layers of octahedra and of tetrahedra, and they cannot be completely saturated coordinately with oxygen atoms.

Malquori and Cirilli [17] studied the structure of $2CaO \cdot Fe_2O_3$, $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, and $6CaO \cdot 2Al_2O_3 \cdot Fe_2O_3$ by rotation and Weissenberg X-ray diffraction. Table 4 gives the parameters of the lattices (in Angstrom units).

The elementary cell of dicalcium ferrite contains four molecules of $2CaO \cdot Fe_2O_3$ ($Ca_8Fe_4^{IV}Fe_4^{VI}O_{20}$). Nonequivalence of iron atoms along the b axis is found. In the elementary cell of $2CaO \cdot Fe_2O_3$ iron atoms are found in tetrahedral and octahedral coordination with formation of groupings FeO_6, FeO_4, FeO_6, FeO_4 arranged along the b axis and united together through oxygen atoms. In the a direction these groups must be united to analogous groups. The Ca ions are arranged in the same plane (parallel to ac) as the oxygen atoms through which FeO_6 and FeO_4 groups are united.

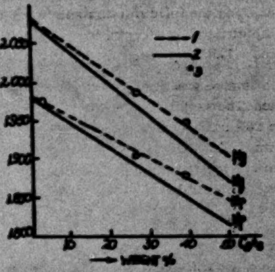
TABLE 1

Sample No.	Composition of sample		Refractive indices calculated on the assumption that $5CaO \cdot 3Al_2O_3$ enters into solid solution in the form of					
	$5CaO \cdot 3Al_2O_3$, wt. %	$5CaO \cdot 3Al_2O_3$, mole %	the cubic modification			the rhombic modification		
			N_g	N_p	$N_g - N_p$	N_g	N_p	$N_g - N_p$
1	10	8.5	2.04	1.949	0.091	2.047	1.955	0.092
2	20	17.2	2.00	1.917	0.083	2.013	1.93	0.083
3	30	26.2	1.957	1.884	0.073	1.978	1.903	0.075
4	40	35.6	1.913	1.848	0.065	1.942	1.875	0.067
5	50	45.0	1.869	1.813	0.056	1.904	1.846	0.058

TABLE 2

Sample No. *	CaO, wt. %	Al_2O_3, wt. %	Fe_2O_3, wt. %	Al_2O_3/ Fe_2O_3 (alumina modulus)
12	50.0	38.0	12.0	3.17
14	49.73	36.27	14.0	2.59
16	49.4	34.6	16.0	2.162
20	48.6	31.4	20.0	1.57
24	47.8	28.2	24.0	1.175
32	46.32	21.68	32.0	0.68
42	44.43	13.57	42.0	0.32

* The Sample No. corresponds to the ferric oxide content of the sample.



Graphs for the dependence of the refractive indices of aluminoferrites on the amount of C_5A_3 going into solid solution with C_4AF.

The elementary cells of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ and $2CaO \cdot Fe_2O_3$ belong to the type $Ca_8Me_4^{IV}Me_4^{VI}O_{20}$, in which $Me^{IV}Me^{VI}$ denotes iron or aluminum atoms having coordination numbers of 4 and 6. The relative numbers of atoms in the elementary cell of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ can be expressed as $Ca_8Fe_4^{IV}Al_4^{VI}O_{20}$, in which iron is in the tetrahedral formand aluminum in the octahedral state of coordination. The relative numbers of atoms in the elementary cell of $2CaO \cdot Fe_2O_3$ can be expressed as $Ca_8Fe_4^{IV}Fe_4^{VI}O_{20}$, in which Fe_4^{IV} and Fe_4^{VI} are iron atoms having coordination numbers of 4 and 6, respectively. For the composition $6CaO \cdot 2Al_2O_3 \cdot Fe_2O_3$ (22.8 % of ferric oxide), given by Swayze, and also for the composition $6CaO \cdot 2.1Al_2O_3 \cdot 0.9Fe_2O_3$ (20.7% of ferric oxide), given by Malquori, it did not appear to be possible to assign positions of atoms in an elementary cell of the type $Ca_8Me_4^{IV}Me_4^{VI}O_{20}$. It must therefore be considered that Swayze's formula merely gives the proportions of the three oxides.

As regards the structure of the solid solution having the maximum content of aluminate, as determined in this investigation, we must make the following remarks. It is probable that the relative numbers of atoms in the elementary cell of the solid solution of limiting composition can be expressed in the form $Ca_8Fe_2Al_6O_{20}$, corresponding to the type $Ca_8Me_4^{IV}Me_4^{VI}O_{20}$, which is common to $2CaO \cdot Fe_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. In fact, the limiting composition of the solid solution, which we have given in the form $6CaO \cdot 2.49Al_2O_3 \cdot 0.77Fe_2O_3$, can be expressed as $7.8CaO \cdot 3.24Al_2O_3 \cdot Fe_2O_3$, a coefficient of unity being taken for ferric oxide. This formula can be expressed approximately as $8CaO \cdot 3Al_2O_3 \cdot Fe_2O_3$ ($Ca_8Fe_2Al_6O_{20}$). In all probability for such a composition a

TABLE 3

Sample No.	Refractive indices of aluminoferrites			Composition of aluminoferrites				Formulas of aluminoferrites***	Fe_2O_3 content of aluminoferrite, % by wt.	Ratio $\frac{CaO}{Al_2O_3+Fe_2O_3}$
	N_g	N_p	N_g-N_p	C_5A_3,* wt. %	C_4AF,** wt. %	C_5A_3, mol. %	C_4AF, mol. %			
12	1.914	1.854	0.06	47.5	52.5	42.8	57.2	$7.8CaO\cdot 3.24Al_2O_3\cdot 177Fe_2O_3$	17.2	1.84
14	1.914	1.854	0.06	47.5	52.5	42.8	57.2	$7.8CaO\cdot 3.24Al_2O_3\cdot 1.77Fe_2O_3$	17.2	1.84
16	1.923	1.863	0.06	44.5	55.5	40.25	59.75	$7.33CaO\cdot 2.98Al_2O_3\cdot 1.82Fe_2O_3$	18.2	1.84
20	1.946	1.876	0.068	39.0	61.0	34.6	65.4	$6.7CaO\cdot 2.59Al_2O_3\cdot 1.9\ Fe_2O_3$	20.0	1.86
24	1.983	1.900	0.083	29.9	70.1	26.15	73.85	$5.77CaO\cdot 2.06Al_2O_3\cdot 1.04Fe_2O_3$	23.0	1.92
32		1.973		2.86	97.14	2.39	97.61	$4.12CaO\cdot 1.07Al_2O_3\cdot 1.45Fe_2O_3$	31.8	2.0

* Abbreviation for $5CaO\cdot 3Al_2O_3$

** Abbreviation for $4CaO\cdot Al_2O_3\cdot Fe_2O_3$

*** A coefficient of unity is assumed for ferric oxide.

TABLE 4

Composition of crystals	a_0	b_0	c_0
$2CaO\cdot Fe_2O_3$	5.32	14.63	5.58
$4CaO\cdot Al_2O_3\cdot Fe_2O_3$	5.26	14.42	5.51
$6CaO\cdot 2Al_2O_3\cdot Fe_2O_3$	5.22	14.35	5.48

TABLE 5

Composition	Fe_2O_3, wt. %	No. of molecules in elementary cell	Structural formula (type $Ca_8Me_4^{IV}Me_4^{VI}O_{20}$)
$2CaO\cdot Fe_2O_3$	58.8	4	$Ca_8Fe_4^{IV}Fe_4^{VI}O_{20}$
$4CaO\cdot Al_2O_3\cdot Fe_2O_3$	32.8	2	$Ca_8Fe_4^{IV}Al_4^{VI}O_{20}$
$8CaO\cdot 3Al_2O_3\cdot Fe_2O_3$	17.5	1	$Ca_8Fe_4^{IV}Al_2^{IV}Al_4^{IV}O_{20}$

TABLE 6

Alumina moduli of clinkers	N_g	N_p	N_g-N_p
Clinker from Bakin works	1.942	1.888	0.054
Clinker from Shchurov works	1.959	1.900	0.059
Clinker from Kuvasai works	1.929	1.881	0.048

certain amount of calcium oxide will be held in solid solution. This composition can be taken to be the final member of a series of solid solutions of aluminoferrites; it contains 17.5% by weight of ferric oxide. By the method of crystal optics we have found the value of 17.2% by weight of ferric oxide for such a solid solution. Comparison of these results shows that agreement is quite satisfactory. It is probable that one molecule of $8CaO\cdot 3Al_2O_3\cdot Fe_2O_3$ is contained in the elementary cell of the limiting solid solution.

Büssem considers that in the solid solution the aluminum atoms occur only in the octahedral coordination, a view which he based on the structure of tetracalcium aluminoferrite ($Ca_8Fe_4^{IV}Al_4^{VI}O_{20}$). We think that the views of Malquori and Cirilli are more correct, namely, that in aluminoferrites aluminum atoms can have coordination numbers of 6 and 4. In fact, the existence of an aluminoferrite solid solution of the type $Ca_8Fe_2Al_6O_{20}$ confirms this view. Aluminum atoms occur here in tetrahedral (4 atoms) and in octahedral (2 atoms) coordinations. On the basis of the general type $Ca_8Me_4^{IV}Me_4^{VI}O_{20}$, the limiting composition of the solid solution can be represented as $Ca_8Fe_2^{IV}Al_2^{IV}Al_4^{VI}O_{20}$. Table 5 gives members of the series of solid solutions of aluminoferrites together with suggested structural formulas.

The general formula for all three compositions has the form $8CaO\cdot xAl_2O_3\cdot yFe_2O_3$, in which x varies from 0 to 3 and y from 4 to 1, and the sum x + y = 4.

Solid Solutions in the System $3CaO\cdot Al_2O_3 - 4CaO\cdot Al_2O_3\cdot Fe_2O_3$. The question of the formation of solid solutions between $3CaO\cdot Al_2O_3$ and $4CaO\cdot Al_2O_3\cdot Fe_2O_3$ has not been resolved.

Thus, there are indications in the literature of the formation of solid solutions between tricalcium aluminate and tetracalcium aluminoferrite. McMurdie [5] considers that $3CaO\cdot Al_2O_3$ is soluble to the extent of 2.5-5 % by weight. A discussion of the solubility of $3CaO \cdot Al_2O_3$ in $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ has been given by Toropov and Merkov [18]. The elucidation of this matter is of great importance for the structure of clinker. The study of this system is complicated by the incongruent melting of $3CaO \cdot Al_2O_3$.

In the system $3CaO \cdot Al_2O_3 - 4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ we have studied three compositions having different alumina moduli (Al_2O_3/Fe_2O_3 ratios):

1) 50% $3CaO \cdot Al_2O_3$ and 50% $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, $Al_2O_3/Fe_2O_3 = 1.786$
2) 60% $3CaO \cdot Al_2O_3$ and 40% $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, $Al_2O_3/Fe_2O_3 = 2.361$
3) 70% $3CaO \cdot Al_2O_3$ and 30% $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, $Al_2O_3/Fe_2O_3 = 3.314$

In the optical study of these samples in transmitted and reflected light the interesting fact emerged that all three samples contained not only $3CaO \cdot Al_2O_3$, $5CaO \cdot 3Al_2O_3$, and aluminoferrite, but also free calcium oxide. The presence of free calcium oxide can be explained on the assumption that it is not $3CaO \cdot Al_2O_3$ that enters into solid solution with $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, but $5CaO \cdot 3Al_2O_3$, since tricalcium aluminate decomposes when melted. As regards pentacalcium trialuminate, it not only melts without decomposition, but, as Kazumi Mori and Yukio Matsushita supposed [19], it forms associations corresponding to the composition $5CaO \cdot 3Al_2O_3$ in the molten condition.

Finally, we consider that the experiments of Skue [20], carried out at the Institute of Silicate Chemistry on the effect of fluorine compounds on solid solutions of calcium aluminoferrites, provide direct confirmation of the view that $5CaO \cdot 3Al_2O_3$ enters into the composition of the solid solutions of aluminoferrites. Skue showed that, when mixtures of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ and $6CaO \cdot 2Al_2O_3$ are heated with calcium fluoride, it is always $5CaO \cdot 3Al_2O_3$ that separates, not $3CaO \cdot Al_2O_3$, together with aluminoferrite having an alumina modulus less than those of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ and $6CaO \cdot 2Al_2O_3 \cdot Fe_2O_3$.

In the mixtures that we investigated the refractive indices of the aluminoferrites attained the values. $N_g = 1.978$ and $N_p = 1.916$. The investigation was made in sodium light in phosphorus immersion liquids.

Aluminoferrites of Industrial Cement Clinkers. As synthetic aluminoferrites are of variable composition, there is reason to suppose that the actual crystals of the aluminoferrite phase of industrial clinkers will be merely one or another of the above-described series of solid solutions. With the object of determining the composition of the aluminoferrite phase, the so-called "heavy" fractions were separated from three samples of industrial clinker. The separation was effected by centrifugation in methylene iodide. Investigation of the "heavy" fractions with the aid of the microscope and of X-rays showed that aluminoferrites of variable composition were present (Table 6).

This fact has great practical importance. Until now, mineralogical composition of clinker has been calculated on the assumption that only $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ is formed in it. We consider that in the quantitative determination of the minerals of clinker, and of its ferrite component in particular, it is necessary to take microscopic investigation as the main basis of the work. Calculation of the mineralogical composition must take account of the formation of an aluminoferrite whose composition will vary from $8CaO \cdot 2Al_2O_3 \cdot 2Fe_2O_3$ (4 : 1 : 1) and $8CaO \cdot 3Al_2O_3 \cdot Fe_2O_3$ and can be determined from refractive index measurements. When this method is used for the determination of aluminoferrites in clinker, the accuracy with which the other clinker minerals can be determined is increased. This is very important in the diagnosis of the properties of cement, such as strength, sulfate-stability, etc. A study of the aluminoferrites crystallizing from mixtures containing calcium aluminates and silicates and from mixtures containing an excess of free calcium oxide confirmed that they are of variable composition.

SUMMARY

1. Solid solutions of calcium aluminoferrites are formed with the participation not of the cubic form of $5CaO \cdot 3Al_2O_3$, but of rhombic (α') form (which is structurally closer to $2CaO \cdot Fe_2O_3$ and to $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$) the other components being dicalcium ferrite and a certain amount of free calcium oxide.

2. The composition of the aluminoferrite containing the maximum amount of aluminate in solid solution corresponds to 17.5% by weight of ferric oxide. The formula of such an aluminoferrite can be written $8CaO \cdot 3Al_2O_3 \cdot Fe_2O_3$.

3. $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ does not form solid solutions containing $3CaO \cdot Al_2O_3$.

4. Aluminoferrites present in mixtures containing calcium aluminates, calcium silicates, or excess free calcium oxide are of variable composition.

5. The aluminoferrites of industrial clinkers are of variable composition.

6. Calculation of the mineralogical composition of clinker must take into account the formation of an aluminoferrite of the composition indicated by the results of microscopic investigation. This procedure increases the accuracy with which the contents of other clinker minerals can be calculated.

LITERATURE CITED

[1] H. S. Hansen, L. T. Brownmiller and R. H. Bogue, J. Am. Chem. Soc., 50 398 (1928).

[2] T. M. Lea and T. Parker, Phil. Trans. of Royal Soc. London, 731, V. 234, p. 1.

[3] A. Guttman and F. Gille, Zement, 16, p. 500, 1929.

[4] N. A. Toropov, L. D. Merkov, and N. A. Shishakov, Cement, No. 1 1937, p. 28.

[5] H. F. McMurdie, J. of Research of the Natl. Bur. of Stand.,18, 475 (1937).

[6] T. Jamauchi, J. of the Japan Cer. Assoc. 45, 279 (1937); 46, 66 (1938).

[7] E. Newman, J. of Research 38, 661 (1947).

[8] M. Swayze, Am. J. Sci., 244, No. 1-2 (1946), p. 1-30 p. 65-94.

[9] G. L. Malquori and V. Cirilli, Ricerca Sci., 11, 316 (1940); 14, 78 (1943).

[10] V. Cirilli and A. Burdese, Ricerca Sci., 21, 1185 (1951).

[11] V. Cirilla and C. Brisi, Annali di chimica, 41, 61 (1951), No. 1.

[12] D. S. Belyankin, B. V. Ivanov, and V. V. Lapin, Petrography of Technical Stone, 1952, p. 457.

[13] S. Solacolu, Zement, 1932, V. 21, p. 301.

[14] T. W. Parker, Third International Symposium on the Chemistry of Cement, London, 1952.

[15] N. L. Bowen and J. Schairer, Am. J. Sci., p. 151, 1935.

[16] W. Büssem, Fortschritte der Mineralogie, Kristallographie and Petrographie, 1937, V. 22, p. 31; Proceedings of Symposium on Chemistry of Cements, Stockholm, 1937, p. 153.

[17] G. L. Malquori and V. Cirilli, Third International Symposium on the Chemistry of Cement, London,1952.

[18] N. A. Toropov and L. D. Merkov, Cement, 1939, No. 3, p. 43.

[19] Kazumi Mori and Vukio Matsushita, C. A., 53, 12169 f; Tetsuto-Hagane, 38, 531-6, 1952.

[20] N. A. Toropov and E. R. Skue, Proc. Acad. Sci., USSR, 1954, V. 88, No. 3, p. 415-418.

Received May 3,1955

Institute of Silicate Chemistry of the
USSR Academy of Sciences

BLANK
PAGE

KINETICS OF BROMINE EXCHANGE IN COMPLEX PLATINUM BROMIDES

A. A. Grinberg and G. A. Shagisultanova

The compounds used in the first study of isotopic exchange in complex compounds in 1939 [1] were complex platinum bromides, in particular, $K_2[PtBr_4]$ and $K_2[PtBr_6]$. It was shown that exchange occurs at a measurable rate in these compounds and that all of the bromine atoms take part in the exchange. In the intervening fifteen years exchange phenomena in complex compounds has been the subject of several investigations both in the USSR and in other countries.

Until recently, however, these investigations have not been closely concerned with the kinetics of the exchange processes. The gathering of kinetic data, i.e. data for the dependence of the exchange rate on the concentration of reactants and on other factors, was begun by Adamson [2], who worked with the complex cyanide $K_3[Mn(CN)_6]$. The first tentative data on the activation energies of exchange reactions of complex platinum compounds were obtained by the present authors in collaboration with Nikolskaya and Kozlova [3].

In the present investigation we have studied the kinetics of exchange in $K_2[PtBr_4]$ and $K_2[PtBr_6]$, the variables examined being time, concentration of complex ion, concentration of free ligand (Br^-), and temperature. Further experiments were carried out to determine the effect of sunlight on the exchange rate.

EXPERIMENTAL

The procedure was as follows. Active bromine was obtained from irradiated bromobenzene, which was shaken with aqueous KBr, the aqueous layer being then extracted with benzene in order to free it from the organic component. A weighed amount of the pure preparation of complex salt ($K_2[PtBr_4]$ or $K_2[PtBr_6]$) was dissolved in a definite volume of water, and to this solution a solution of KBr of definite concentration and containing Br^{82} tracer was added. The solution was stirred for a definite time at a given temperature in a thermostat protected from the action of light and the complex ion was then separated almost completely from solution by the addition of a suitable precipitant. The $[PtBr_4]^{--}$ ion was precipitated as $[Pt(NH_3)_4][PtBr_4]$ or $[Ni(En)_3][PtBr_4]$. The $[PtBr_6]^{-}$ ion was precipitated as $Cs[PtBr_6]$. The compositions of the precipitated salts and the completeness with which they were separated were established by control experiments, and it was shown by further control experiments that it was unnecessary to make a correction for "zero" (induced) exchange.

After being washed, the precipitated salts were brought into solution, and their activities were measured with a suitable counting arrangement. $[Pt(NH_3)_4][PtBr_4]$ was brought into solution by means of hot caustic alkali, $[Ni(En)_3][PtBr_4]$ also by means of alkali, and $Cs2[PtBr_6]$ by treatment with dilute $Na_2S_2O_3$ solution. Measurements were made not only on the solution of the complex, but also on the mother liquor and on a standard solution ($KBr + KBr^{82}$). The activity balance sheet (adjusted to a given time) was extremely satisfactory. For example, in one experiment the activity of the solution of the complex together with that of the mother solution was 752, whereas the activity of the standard was 766 (all activities are given in impulses per minute). Our results are detailed below.

1. Dependence of Degree of Exchange on Time. As usual, we employ the term "degree of exchange" to mean $I = \frac{x_t}{x_\infty}$, in which x_t is the activity of the complex at time t (from the start of the experiment), and x_∞ is attained In Fig. 1, time (minutes) is plotted along the axis of abscissae and $\frac{x_t}{x_\infty}$. 100% along the axis of ordinates for $K_2[PtBr_4]$ and for $K_2[PtBr_6]$. In these experiments the concentration of the complex ion was $0.55 \cdot 10^{2}$ mole/liter in each case, and the KBr concentration was $2.2 \cdot 10^{-2}$ mole/liter in the case of $K_2[PtBr_4]$ and $3.3 \cdot 10^{-2}$ mole/liter in the case of $K_2[PtBr_6]$.

In Figures 2 and 3, time (minutes) is again plotted as abscissa, and the ordinate is the negative natural logarithm of $(1-F)$; Fig. 2 refers to $K_2[PtBr_4]$, and Fig. 3 to $K_2[PtBr_6]$. The points in Fig. 1 correspond to separate experiments but those in Figures 2 and 3 represent the averaged results of a whole series of separate experiments.

2. Dependence of the Degree of Exchange on the Concentrations of Reactants. Fig. 4 shows the dependence of the degree of exchange $\frac{x_t}{x_\infty}$ 100% on the concentration of $K_2[PtBr_4]$. In all of the experiments of this series the

KBr concentration was kept constant at $2.2 \cdot 10^{-2}$ mole/liter. The experiments were carried out at 20°, and the duration of the exchange reaction was about ten minutes. Fig. 5 shows the dependence of the degree of exchange on KBr concentration. In all of the experiments of this series the concentration of $K_2[PtBr_4]$ was $0.55 \cdot 10^{-2}$ m/l, the temperature was 20°, and the duration of the exchange reaction was 30 minutes. Figures 6 and 7 show the analogous relationships for $K_2[PtBr_6]$. In the experiments illustrated by Fig. 6, the KBr concentration was $3.3 \cdot 10^{-2}$ mole/liter, the temperature was 20°, and the duration of the exchange reaction was about 30 minutes. In the experiments illustrated by Fig. 7 the concentration of $K_2[PtBr_6]$ was $0.77 \cdot 10^{-2}$ mole/liter.

3. Dependence of the Degree of Exchange on Temperature. In Fig. 8 temperature is plotted as abscissa and degree of exchange as ordinate for $K_2[PtBr_4]$ and $K_2[PtBr_6]$. Figure 9 differs from Fig. 8 in that the natural logarithm of the degree of exchange is plotted as ordinate.

4. Dependence of the Degree of Exchange on the "Age" of the Solution. After most of the results given above had been obtained, a new effect was discovered, it being found that the degree of exchange depends on the "age" of the solution of the complex, i.e. on the time elapsing from the preparation of the solution to the start of the exchange experiment. This effect was detected in $K_2[PtBr_4]$ solutions. In solutions that were let stand, the degree of exchange was greater than in freshly prepared solutions, other conditions remaining constant. Our results are given in the table. Preliminary experiments showed that a similar effect occurs to some extent in the case of $K_2[PtBr_6]$. After we had discovered this effect we learnt that a similar phenomenon had been observed independently by Adamson and Wilkins [4] for thiocyanato-pentammines of cobalt and chromium.

5. Effect of Light. As already stated, the exchange experiments described above were carried out in a thermostat protected from the action of light. It was shown by special experiments that for $K_2[PtBr_4]$ the same results are obtained whether the exchange reaction occurs in the light or in the dark.

Light has an appreciable effect on bromine exchange in K_2PtBr_6. Thus, at a K_2PtBr_6 concentration of $0.55 \cdot 10^{-2}$ mole/liter and a KBr concentration of $3.3 \cdot 10^{-2}$ mole/liter (at 20° for 30 minutes) the extent of exchange is on the average 30% in the dark, but is appreciably higher, varying from 45% to 75% in individual cases, in the light. The variation observed may be due to variation in the intensity of illumination in different experiments. The effect of light on bromine exchange in K_2PtBr_6 is under further investigation.

DISCUSSION OF RESULTS

It must be pointed out that the values that we have obtained for the exchange rate in dilute solutions of $K_2[PtBr_4]$ are appreciably lower than those obtained in the first investigation by Grinberg and Filinov [1]. This discrepancy may be attributed in part to the increased accuracy of measurement now possible, as compared to that possible in 1939. However, this is probably not the only factor concerned. Rich and Taube [5] recently pointed out the important part played by impurities, which may have a catalytic effect on the exchange. We are studying this matter further at the present time. In the present work, however, $K_2[PtBr_4]$ was prepared on many occasions and all of the samples behaved identically.

Comparison of the data given in this paper with that of Grinberg and Nikolskaya [6] brings out clearly the high degree of dependence of the exchange rate of $K_2[PtBr_4]$ on the total concentration of atoms undergoing exchange. In fact, according to the results of Grinberg and Nikolskaya [6], the time for the practical attainment of equilibrium is about 40 minutes for $C_{K_2PtBr_4} = 0.5 \cdot 10^{-1}$ mole/liter and $C_{KBr} = 2 \cdot 10^{-1}$ mole/liter, the half-exchange period calculated from these results being about 7-9 minutes; on the other hand, according to Fig. 1 the half-exchange period for $K_2[PtBr_4]$ ($C = 0.55 \cdot 10^{-2}$ mole/liter) is 120 minutes (Fig. 10).

When we take into account the qualitative character of the results obtained previously and the absence of thermostatic control in the experiments of Grinberg and Nikolskaya, we can undoubtedly conclude that the half-exchange period of $K_2[PtBr_4]$ is highly dependent on the total concentration of the atoms undergoing exchange. The form of this dependence appears to be close to that required for a bimolecular reaction. It will be seen from Figures 1 and 2 that, under the conditions studied, the exchange process in $K_2[PtBr_4]$ is satisfactorily described by the fundamental equation for simple exchange, i.e.

$$-\ln(1-F) = Rt\frac{a+b}{ab}$$

For the given temperature conditions and concentrations (see Figures 1 and 2) R is close to $0.5 \cdot 10^{-4}$ g-atom of bromine per liter per minute. By dividing this value by the molar concentration of the complex, we arrive at the value of $K = \frac{R}{C}$. As regards the variation in the extent of exchange with $K_2[PtBr_4]$ with time, however, there is some departure from the usual exponential relationship. The way in which the extent of exchange increases with time indicates the possibility of the participation of a chain mechanism in the process. In this case it is not possible, in general, to calculate the value of R on the basis of the law of simple exchange. However, an approximate tentative value of R can be obtained on the assumption that in this case $\ln(1-F)$ is a linear function of time. This tentative calculation gives values of R of the order of $2\text{-}3 \cdot 10^{-4}$ g-atom of bromine per liter per minute. In any case it is clear that the exchange rate in $K_2[PtBr_4]$ is considerably higher than in $K_2[PtBr_6]$. The graphs given above show that at a concentration of the complex of $0.55 \cdot 10^{-2}$ mole / liter and at 20°, the half-exchange period for $K_2[PtBr_6]$ is about 120 minutes, whereas for $K_2[PtBr_4]$ it is about 50 minutes (see Fig. 10). With respect to the extent of breakdown into ions, $[PtBr_6]^{--}$ must be more stable than $[PtBr_4]^{--}$. Hence, we again meet with the fact, established previously, that the degree of instability (instability constant) of a complex is not bound in any way to determine the rate with which it undergoes exchange. We shall return to this question later.

The graphs indicate that the degree of exchange, both of $K_2[PtBr_4]$, and of $K_2[PtBr_6]$, is approximately proportional to the concentration of the complex under the conditions studied. A simple relationship of this kind is to be expected when the comparatively low degrees of exchange are taken into account. It cannot be doubted that the linear relationship between the degree of exchange and the concentration of the complex represents a first approximation. This view is confirmed by experiments that we have carried out recently: at higher concentrations of $K_2[PtBr_4]$ the exchange rate is probably proportional not to the first power of this concentration, but to a higher power.

As regards the dependence of the degree of exchange on the concentration of free ligand (Br^-), it is almost absent in the case of $K_2[PtBr_4]$, but is very marked in the case of $K_2[PtBr_6]$. This fact again emphasizes the undoubted difference in the mechanism of exchange in such closely related complex compounds as $K_2[PtBr_4]$ and $K_2[PtBr_6]$. When the above-mentioned newly discovered effect is taken into account, the almost complete independence of the degree of exchange in $K_2[PtBr_4]$ on the KBr concentration may be explained on the assumption that the exchange rate is determined by the rate of a slower aquation process. The rate at which bromide ions enter and leave the inner sphere is apparently much greater than the rate of the primary interaction of the $[PtBr_4]^{--}$ ion with water. Our results indicate that, in the dilute solutions studied, the mechanism of reaction via intermediate formation of $K_3[PtBr_5]$ plays a very small part in comparison with that of reaction via aquo ions.

As regards $K_2[PtBr_6]$, it is probable that exchange by an oxidation-reduction mechanism plays an important part. Many years ago Grinberg, Ptitsyn, and Lavrentyev [7] showed that hexahaloplatinates $K_2[PtX_6]$ dissociate in solution with liberation of free halogen in accordance with the equation $K_2[PtX_6] \rightleftarrows K_2[PtX_4] + X_2$. For differing X (Cl, Br, SCN, I) the degree of dissociation differed, increasing from chlorine to iodine. For $K_2[PtBr_6]$ the equilibrium bromine concentration determined from the oxidation-reduction potential is about 10^{-14}; for $K_2[PtI_6]$ the equilibrium iodine concentration is 10^{-5}.

It is characteristic of hexahaloplatinates that their stabilities with respect to breakdown into ions increase from chlorine to iodine, whereas their thermal stabilities decrease in this direction. The dependence of the degree of exchange on the KBr concentration, the tentative values of activation energy given below, and also the experimentally established high degree of dependence of the extent of exchange on the intensity of illumination are all in accord with the view that an oxidation-reduction mechanism plays an important part in the exchange of $K_2[PtBr_6]$ with bromide ions.

Earlier investigations by Grinberg and Filinov [8] showed that the interaction of compounds of a given metal in different stages of oxidation often passes through a stage of intermediate compounds of the quinhydrone type. Thus, by careful oxidation of $[Pt(NH_3)_2Br_2]$ under suitable conditions, or by careful reduction of $[Pt(NH_3)_2Br_4]$, it is easy to isolate "molecular" compounds of the type $[Pt(NH_3)_2Br_2]$. $[Pt(NH_3)_2Br_4]$. The existence of such compounds has been established in the majority of cases. It is quite possible that products of a similar type are formed also during the reduction of $K_2[PtBr_6]$. In fact, it is difficult to imagine the elimination of a Br_2 molecule from $K_2[PtBr_6]$ as an elementary act. It is obvious that a single atom of bromine must first split off with the intermediate formation (very transitory, possibly) of a tervalent platinum derivative in accordance with the scheme: $[PtBr_6]^{--} \rightleftarrows [PtBr_5]^{--} + Br^\bullet$. The $[PtBr_5]^{--}$ ions must be unstable. They may decompose according to the scheme: $2PtBr_5 \rightleftarrows [PtBr_6] \rightleftarrows [PtBr_4]^{--}$. The atomic bromine eliminated may react with the solvent according to the schemes: $Br^\bullet + H_2O \rightleftarrows HBr + OH$ and $Br^\bullet + H_2O \rightleftarrows OHBr + H$, and it may react also with bromide ions. The probability of the last reaction increases as the KBr concentration is increased. We may here postulate the formation of the simplest polyhalide ion Br_2^-.

The intermediate formation of ions of the type $[PtCl_5]^{--}$ was postulated by Rich and Taube [5] in a recently published paper, in which they make no mention of our investigations on the interaction of compounds of a given metal in different states of oxidation, nor of our work on chlorine exchange in the $[PtCl_6]^{--}$ ion.

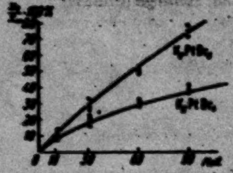


Fig. 1.

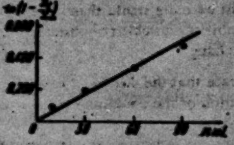


Fig. 2.

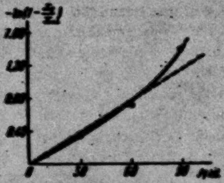


Fig. 3.

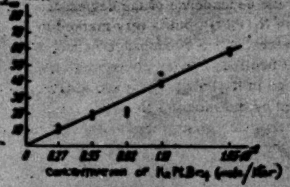


Fig. 4.

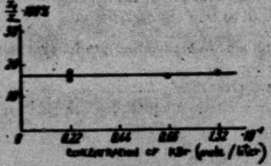


Fig. 5.

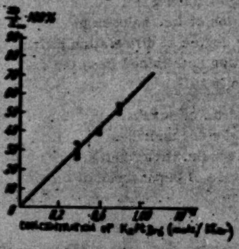


Fig. 6.

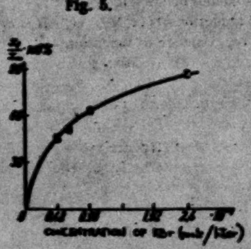


Fig. 7.

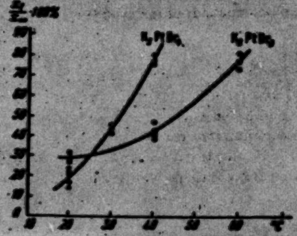


Fig. 8.

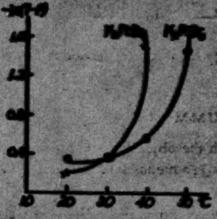


Fig. 9

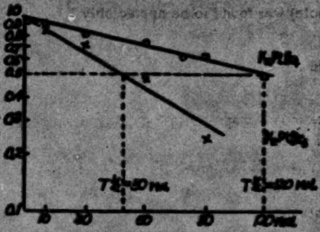


Fig. 10

TABLE

Time from moment of dissolution to start of exchange	Activity of complex (without background) (impulses/ minute)	Activity of standard (without background) (impulses/ minute)	$\frac{x_t}{x_\infty}.100\%$	$1-\frac{x_t}{x_\infty}$
10—15 minutes	152	1410	21	
	204	2700	16 av. 18±7	0.82
	500	5720	17	
24 hours	635	3824	33	
	468	2640	35 av. 35±6	0.65
	500	2600	38	
48 hours	340	1730	40	
	360	1732	42 av. 41±7	0.59

We do not assert that exchange in $K_2[PtBr_6]$ occurs exclusively by an oxidation-reduction mechanism, but we emphasize the importance of the part played by this process in the general (possibly more complex) process.

Tentative calculations of activation energies were made with the aid of the Arrhenius equation:

$$E = \frac{2.3\ RT_1T_2}{T_2 - T_1} \quad \log \frac{K_2{}^{*}}{K_1}.$$

According to our results, the activation energy for $K_2[PtBr_4]$ is about 17 kcal/ mole, and that for $K_2[PtBr_6]$ varies from 4 to 10 kcal/ mole.

SUMMARY

1. Experimental data have been obtained with the object of elucidating the dependence of the extent of isotopic exchange of bromine in $K_2[PtBr_4]$ and $K_2[PtBr_6]$ (aqueous solutions) on the duration of the exchange reaction, the concentration of the complex ion, the concentration of bromide ions, the temperature, and the presence of sunlight. An exchange-acceleration effect was detected in aqueous solutions of $K_2[PtBr_4]$ that had been allowed to stand.

2. On the basis of the data obtained, tentative calculations were made of the activation energies of the exchange process in the $[PtBr_4]^{--}$ and $[PtBr_6]^{--}$ ions. Under the conditions studied the activation energy for bromine exchange in the $[PtBr_6]^{--}$ ion (4-10 kcal/ mole) was found to be appreciably less than the activation energy for the $[PtBr_4]^{--}$ ion (about 17 kcal/ mole).

3. On the basis of the data obtained it is concluded that the mechanism of the exchange reaction is different in the $[PtBr_4]^{--}$ and $[PtBr_6]^{--}$ ions.

4. Over the concentration range studied, exchange with $K_2[PtBr_4]$ in aqueous solution proceeds to a large extent though the intermediate formation of aquo ions.

5. The character of the dependence of the degree of exchange on the bromide ion concentration, the values obtained for the activation energy, the effect of sunlight on the degree of exchange, and also some previously studied properties of quadrivalent platinum derivatives enable us to postulate that exchange with $K_2[PtBr_6]$ proceeds mainly via an oxidation-reduction equilibrium.

6. The data obtained in this work for the $[PtBr_4]^{--}$ and $[PtBr_6]^{--}$ ions again confirm the conclusion first reached by Grinberg and Nikolskaya, namely, that the instability of a complex ion, as measured by its instability constant, by no means always determines the rate at which it undergoes exchange.

LITERATURE CITED

[1] A. A. Grinberg and F. M. Filinov, Proc. Acad. Sci. USSR 623, 912 (1939).

[2] A. W. Adamson, L. P. Welker, W. B. Wright, J. Am. Chem. Soc., 73, 3786 (1951).

[3] A. A. Grinberg, L. I. Kozlova, L. E. Nikolskaya and G. A. Shagisultanova, J. Appl. Chem. 28, No. 1, 1955 (T.p. 5)*.

[4] A. W. Adamson and R. G. Wilkins, J. Amer. Chem. Soc., 76, 3379 (1954).

[5] R. Rich, H. Taube, J. Am. Chem. Soc., 76 2608 (1954).

[6] A. A. Grinberg and L. E. Nikolskaya, J. Appl. Chem. 22, 542 (1949); J. Appl. Chem. 9, 893 (1951) (T.p. 1027)*

[7] A. A. Grinberg, B. V. Ptitsyn, and V. N. Lavrentyev, Proc. Acad. Sci., USSR, 26, 51 (1940).

[8] A. A. Grinberg and F. M. Filinov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1245 (1937).

Received May 30 1955

V. G. Khlopin Radium Institute of the
USSR Academy of Sciences

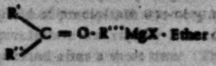
---

* In place of K_2 and K_1 we put values of R from the equation $-\ln(1-F) = Rt\,\frac{a+b}{ab}$.

REACTIONS OF FENCHONE WITH ORGANOMAGNESIUM AND ORGANOLITHIUM COMPOUNDS

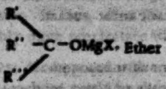
A. N. Nesmeyanov, V. A. Sazonova, and R. B. Materikova

We have shown previously [1] that in the reaction of a Grignard reagent with a carbonyl compound it is not possible to isolate a complex compound of the type.



$$\begin{matrix} R' \\ & C = O \cdot R'''MgX \cdot Ether \\ R'' \end{matrix}$$

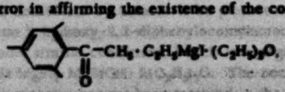
and that the intermediate compounds described by Hess [2], Meisenheimer [3], and others as complexes are of the alkoxide type.



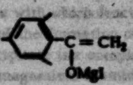
$$\begin{matrix} R' \\ R'' - C - OMgX \cdot Ether \\ R''' \end{matrix}$$

as supposed by Grignard.

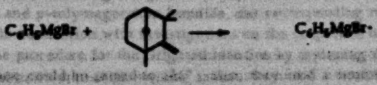
Klages [4] was in error in affirming the existence of the complex.



Fuson and coworkers [5] showed that in this case the substance formed was the enolate of 2', 4', 6'-trimethylacetophenone



and not a complex formed with an organomagnesium compound. There remains the complex of a carbonyl compound, with a Grignard reagent described by Leroide [6], namely, the addition product formed by fenchone with phenylmagnesium bromide



As this case was in conflict with our results and there were independent reasons for doubting it, we set ourselves the task of determining the structure of this compound, the study of which we had undertaken previously but had not completed.

Leroide writes: "Fenchone reacts with aromatic organomagnesium compounds to give addition products that are insoluble in ether and hydrocarbons. When these derivatives are treated with water, fenchone is regenerated and the hydrocarbon corresponding to the organomagnesium compound used is formed. The following compounds were prepared:

$C_6H_5MgBR \cdot C_{10}H_{16}O$; $o\text{-}CH_3C_6H_4MgBr \cdot C_{10}H_{16}O$; $p\text{-}CH_3C_6H_4MgBr \cdot C_{10}H_{16}O$.

By prolonged heating in presence of a large amount of solvent these compounds were converted into magnesium derivatives of tertiary alcohols.".

As the author does not give any analysis, does not discuss the separation of these precipitates, and apparently worked with the reaction mixture, the hydrocarbon that he found in the decomposition products can be accounted for by unchanged organomagnesium compound present in the solution, especially when we take into account the fact that very little precipitate was obtained; there can be no doubt that fenchone also would then be obtained. When the reaction mixture was heated for a long time (80 hours in a mixture of ether and toluene for the phenyl derivative), Leroide succeeded in obtaining small amounts of tertiary alcohols (7% for 2-phenylfenchyl alcohol). There is no proof, however, that these alcohols were formed from the precipitate and not from the fenchone and phenylmagnesium bromide present in the solution.

In our work we tried to avoid the errors made by Leroide. All experiments requiring the absence of oxygen and moisture were carried out in an atmosphere of pure dry nitrogen. The precipitate was filtered off through a sintered glass filter, washed repeatedly with absolute ether, dried in a current of nitrogen, and analyzed. The further work was carried out solely with this precipitate.

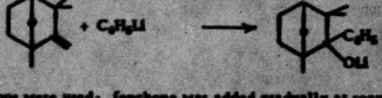
Experiment showed that the analysis of the precipitate was far-moved from that required by Leroide's formula and also from that required by the magnesium derivative of the tertiary alcohol. The Mg : Br ratio found was 1 : 1.4 (Br 40.68%, Mg 8.80%); but for the complex postulated by Leroide we ought to have obtained Br 24.03%, Mg 7.27% (Mg : Br ratio, 1 : 1). The yield of precipitate was very low (3.6%, was calculated as $C_6H_5MgBr\cdot C_{10}H_{16}O$). When the solution filtered from the precipitate was rapidly poured into another vessel in the open air, a further small amount of the same precipitate separated after a short time. The small amount in which this substance was formed, the slow formation of further precipitate when the filtrate was allowed to stand in the air, and the pressure of appreciable amounts of biphenyl in the solution – all these facts suggested that the formation of the precipitate was associated with oxidative processes. In fact, when the reaction was carried out under the usual conditions, without the use of nitrogen, considerably more precipitate was obtained and, moreover, its separation was gradual.

When the substance was decomposed with water, ether and fenchone were obtained, and no benzene was detected. It was found that fenchone could be displaced from the complex by means of benzophenone, but no triphenylmethanol was then formed, though this would be the product of the reaction of benzophenone with the phenylmagnesium bromide considered by Leroide to be present in the complex. Benzil also displaced fenchone from the complex, but again no 2-hydroxy-2,2-diphenylacetophenone was detected (benzilic acid was unexpectedly obtained). It was found that, under similar conditions, benzil rearrangement occurred also when benzil was treated with the basic magnesium salt $MgBr_2\cdot MgBrOH\cdot 2(C_2H_5)_2O$. The occurrence of the benzil rearrangement under the action of such weakly alkaline reagents has not been reported in the literature.

The evident absence of phenylmagnesium bromide in the precipitate, the complex nature of the precipitate as indicated by the ease with which fenchone is separated from it by the action of substituting reagents (water, ketones), and the association of the formation of the precipitate with oxidative processes – all these facts point to the conclusion that the precipitate is a complex of fenchone with a basic magnesium salt [$MgBr_2\cdot MgBrOH\cdot 2C_{10}H_{16}O\cdot(C_2H_5)_2O$] and not with phenylmagnesium bromide as maintained by Leroide. It was found, in fact, that treatment of fenchone with a salt of composition $MgBr_2\cdot MgBrOH\cdot 2(C_2H_5)_2O$, prepared by careful oxidation of an ethereal solution of phenylmagnesium bromide with atmospheric oxygen, results in the formation of a complex containing fenchone which is identical in properties with the precipitate studied.

As stated at the beginning, in the reactions of fenchone with phenylmagnesium bromide, o-tolymagnesium bromide, and p-tolymagnesium bromide, the corresponding tertiary alcohols are obtained only in very low yield. In 1946, in connection with investigations on the properties of terpenes, Nametkin and Obtemperanskaya [7] improved the procedure for the Grignard reaction by replacing diethyl ether by dibutyl ether, so that the reaction temperature could be raised to 110° ; also, they used a twofold excess of phenylmagnesium bromide in the reaction. In this way they succeeded in raising the yield of tertiary alcohol from 7% to 35%.

For the synthesis of 2-phenyl- and 2-p-tolyl-fenchyl alcohols we used organolithium compounds:



Very mild reaction conditions were used: fenchone was added gradually at room temperature to an ethereal solution of phenyl- or p-tolyl-lithium, the mixture was stirred for 30 minutes, and the reaction mixture was decomposed with water. The arylfenchyl alcohols were obtained in good yield (70%).

EXPERIMENTAL

Reaction of Fenchone with Phenylmagnesium Bromide. Fenchone (15.2 g) was added to 53.3 ml of a filtered ethereal solution of phenylmagnesium bromide (0.3395 g of C_6H_5MgBr per ml). A crystalline precipitate (1.2 g) was formed; it was filtered off, washed six times with ether, and dried in a current of nitrogen. When immersed in dry Vaseline under the microscope, the crystals were seen to be regular six-sided plates.

Found %: Br 50.68, Mg 8.80

The precipitate was not soluble in ether, benzene, or dioxane; it was soluble in molten benzophenone and benzil, but reaction occurred with liberation of fenchone. Decomposition of the precipitate with ammonium chloride solution yielded ether and fenchone.

Displacement of Fenchone from the Complex by means of Benzophenone. To 5 g of molten benzophenone 2 g of the precipitate was obtained by reaction of fenchone with phenylmagnesium bromide was added. Frothing occurred, and the precipitate dissolved. The resulting mixture was vacuum-distilled (in a current of nitrogen). At 81° (21 mm) 0.55 g of fenchone came over, and 4.4 g of unchanged benzophenone, m.p. 45°, was recovered; it did not give a red color with concentrated sulfuric acid, which indicated that no triphenylmethanol was present, even as impurity. This again confirms the absence of Grignard reagent in the precipitate.

Reaction of Benzil with the Complex. To 1.1630 g of benzil (m.p. 93°), which was melted in a Claisen flask, 1.7 g of the complex obtained by reaction of fenchone with phenylmagnesium bromide was added gradually. Frothing of the mixture occurred, and this was followed by dissolution of the precipitate in the benzil. The solution assumed a reddish-brown color. In order to effect complete removal of ether, the mixture was heated carefully. At 81° (21 mm) 0.45 g of fenchone came over. The residue was cooled, and 2 N HCl and ether were added. The ether layer was separated, and the aqueous layer was extracted twice with ether. The ether layers were treated with 10% NaOH solution, and the alkaline extract was acidified with concentrated hydrochloric acid. Benzilic acid (0.55 g; m.p. 149°) was obtained. In a mixture test with authentic benzilic acid it showed no depression of melting point.

Preparation of $MgBr_2 \cdot MgBrOH \cdot 2(C_2H_5)_2O$. An ethereal solution of phenylmagnesium bromide prepared from 6 g of magnesium and 39 g of bromobenzene in 120 ml of absolute ether was filtered and transferred to the reaction flask. Air freed from CO_2 was passed very slowly over the surface of the solution. From time to time the stirrer was switched on in order to renew the surface. After three hours large crystals began to be precipitated. The experiment was continued for two days. The crystals were filtered off, washed several times with small amounts of absolute ether until the odor of biphenyl disappeared, and dried in a current of nitrogen. Weight of precipitate 8.4 g.

Found %: Br 52.72, Mg 10.73.

These results are in close accord with Holroyd's formula [8] $MgBr_2 \cdot MgBrOH \cdot 2(C_2H_5)_2O$ and with his experimental results: Br 53%, Mg 10.86%. The dried precipitate was a crystalline powder, insoluble in the usual organic solvents. It warmed up spontaneously in the air. When it was decomposed with water, ether separated.

Action of Fenchone on $MgBr_2 \cdot MgBrOH \cdot 2(C_2H_5)_2O$. Fenchone (11.4 g) and absolute ether (100 ml) were added to 8.55 g of $MgBr_2 \cdot MgBrOH \cdot 2(C_2H_5)_2O$ contained in a bottle with a ground-in stopper. The mixture was shaken for 30 hours. The precipitate was filtered off, washed six times with ether, and dried in a current of nitrogen. The product was a colorless powder smelling of fenchone.

Found %: Br 41.21, Mg 9.33

The complex salt became liquid when exposed to air, and it yielded ether and fenchone when decomposed with water. In its properties (decomposition by water, displacement of fenchone by benzophenone and benzil) it was identical with the substance obtained by reaction of phenylmagnesium bromide with fenchone.

2-Phenylfenchyl Alcohol. The experiment was carried out in an atmosphere of nitrogen. An ethereal solution of phenyllithium prepared from 5 g of lithium, 50 g of bromobenzene, and 100 ml of absolute ether was filtered into a Schlenk vessel. The concentration was determined acidimetrically and found to be 0.0933 g of C_6H_5Li per ml. Into the reaction flask 6.87 g (0.08 mole) of phenyllithium was transferred in the form of the above-described ethereal solution. The solution was stirred, and 10 g (0.065 mole) of fenchone was added through a dropping funnel. The reaction mixture was then stirred at room temperature for 30 minutes. Water was added, and the ether layer was separated, washed with water, and dried with magnesium sulfate. Ether was distilled off, and the residue, vacuum-distilled, yielded 10.6 g (70%) of 2-phenylfenchyl alcohol, b.p. 167-168° (14 mm) (the literature [6] gives 166-167° (13 mm).

2-p-Tolylfenchyl Alcohol. p-Tolyllithium was prepared similarly to phenyllithium from 2 g of lithium, 24 g of p-bromotoluene, and 70 ml of absolute ether. The solution was allowed to stand for a short time and then filtered into a Schlenk vessel. The concentration, found acidimetrically, was 0.0653 g of $CH_3C_6H_4Li$ per ml.

Into the reaction flask, 5.91 g (0.06 mole) of p-tolyllithium was transferred in the form of the ethereal solution, and 7.34 g (0.048 mole) of fenchone was added with stirring; there was a slight evolution of heat. Stirring was continued for a further 30 minutes at room temperature. The reaction mixture was decomposed with water, and the ether layer was separated, washed with water, and dried with magnesium sulfate. Ether was distilled off, and the residue, vacuum-distilled, yielded 8.17 g (69%) of 2-p-tolylfenchyl alcohol, b.p. 177° (15 mm) and m.p. 47-52°.

Found %: C 83.61, H 9.90

$C_{17}H_{24}O$. Calculated %: C 83.61, H 9.84

This tertiary alcohol is readily soluble in the usual organic solvents. The literature [6] gives b.p. 180-181° (15 mm).

SUMMARY

1. The precipitate formed by reaction of phenylmagnesium bromide with fenchone was investigated, and it was shown that, contrary to Leroide's view, this substance is not a complex of fenchone with phenylmagnesium bromide, but is a complex formed between a basic magnesium salt, magnesium bromide and fenchone.

2. 2-Phenyl- and 2-p-tolyl-fenchyl alcohols were prepared in good yield with the aid of organolithium compounds.

LITERATURE CITED

[1] A. N. Nesmeyanov and V. A. Sazonova, Bull. Acad. Sci., USSR, Div. Chem. Sci., No. 4, 5, 499. (1941).

[2] K. Hess, H. Rheinboldt, Ber. 54, 2043 (1921); K. Hess, W. Wustrow, Ann. 437, 256 (1924).

[3] J. Meisenheimer, Casper Ber. 54, 1655 (1921); J. Meisenheimer, Ann. 442, 180 (1925); 446, 73 (1925).

[4] A. Klages, Ber. 35, 2635 (1902).

[5] E. P. Kohler, R. Baltzly, J. Am. Chem. Soc. 54, 4015 (1932); R. C. Fuson, C. H. Fisher, G. E. Ulliot, W. O. Fugate, J. Org. Chem. 4, 111 (1939); R. C. Fuson, W. O. Fugate, C. H. Fisher, J. Am. Chem. Soc. 61, 2362 (1939).

[6] J. Leroide, Comptes rend., 148, 1611 (1909).

[7] S. S. Nametkin and S. I. Obtemperanskaya Bull. Moscow State Univ., No. 3 - 4, 137 (1946).

[8] G. Holroyd, Pr. Chem. Soc. 20, 38 (1904).

Received October 3,1954

M. V. Lomonosov State University, Moscow

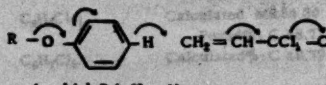
CONDENSATION OF 3,3,3-TRICHLOROPROPENE WITH AROMATIC COMPOUNDS

A. N. Nesmeyanov, R. Kh. Freidlina, and N. A. Semenov

Two authors of this paper have shown, in collaboration with Firstov [1], that 3,3,3-trichloropropene condenses with benzene in presence of a small amount of aluminum chloride with formation of 1,1-dichloro-3-phenylpropene. We considered that this reaction might be of interest as a method of synthesis, permitting the introduction of the reactive grouping $-CH_2CH=CCl_2$, which, in particular, is readily converted into a propionic acid residue — into an aromatic molecule. We have therefore studied the reactions of 3,3,3-trichloropropene with chlorobenzene, bromobenzene, anisole, and phenol.

The reactions of bromobenzene and of chlorobenzene with 3,3,3-trichloropropene in presence of aluminum chloride proceed very vigorously with evolution of heat. The main products isolated were 3-p-bromophenyl-1,1-dichloropropene and 1,1-dichloro-3-p-chlorophenylpropene, respectively. The structures of these products were proved by hydrolysis with concentrated sulfuric acid, which gave good yields of p-bromo- and p-chloro-hydrocinnamic acids, which were then converted into 6-bromo- and 6-chloro-1-indanones. 1,1-Dichloro-3-p-chlorophenylpropene and 3-p-bromophenyl-1,1-dichloropropene add chlorine with formation of 1,1,1,2-tetrachloro-3-p-chlorophenylpropane and 3-p-bromophenyl-1,1,1,2-tetrachloropropane, respectively. The reactions of anisole and phenol with 3,3,3-trichloropropene in presence of aluminum chloride are slower than those of chloro- and bromo-benzenes, and for complete reaction several hours at 80-90° are required. The compound obtained from anisole was found to be 1,1-dichloro-3-p-methoxyphenylpropene, its structure being proved by its oxidation to p-anisic acid with 5% alkaline potassium permanganate. The condensation of 3,3,3-trichloropropene with phenol proceeded when the mixture was heated, even when aluminum chloride was absent, but it was found to be best to carry out the reaction in its presence. Both o- and p-(3,3-dichloroallyl)phenols were isolated. The structures of these compounds were proved by their alkylation with dimethyl sulfate to 1,1-dichloro-3-o-methoxyphenylpropene and 1,1-dichloro-3-p-methoxyphenylpropene, respectively, which were oxidized to the corresponding o- and p-anisic acids. When 1,1-dichloro-3-p-methoxylphenylpropene was hydrolyzed with concentrated sulfuric acid, the product was a p-methoxyhydrocinnamic acid sulfonated in the nucleus, which was isolated as its barium salt. When 3,3,3-trichloropropene reacted with an aqueous solution of sodium phenoxide, both C- and O-alkylation products were formed, the product being a mixture containing o- and p-(3,3-dichloroallyl)phenols together with 1,1-dichloro-3-phenoxypropene.

The same products were obtained when the same aromatic compounds were caused to react with 1,1,3-trichloropropene, but reaction did not occur so readily and the yields were lower than in the reactions with 3,3,3-trichloropropene. The fact that the reaction of 3,3,3-trichloropropene occurs in absence of aluminum chloride is very interesting. In all cases reaction proceeded with allyl rearrangement and formation of compounds containing the 2,2-dichlorovinyl group. The formation of C-derivatives in the reaction of 3,3,3-trichloropropene with phenol and sodium phenoxide obviously proceeded by the mechanism of reaction-center transfer in both of the reacting molecules:



in which R is H or Na.

EXPERIMENTAL

Condensation of Bromobenzene with 3,3,3-Trichloropropene (Preparation of 3-p-Bromophenyl-1,1-dichloropropene). Anhydrous aluminum chloride (1 g) was added to a vigorously stirred mixture of 45 g (0.31 mole) of 3,3,3-trichloropropene and 196 g (1.24 moles) of dry bromobenzene. Vigorous evolution of hydrogen chloride set in, and reaction was complete in 5-10 minutes. The cooled reaction mixture was treated with water, and the lower layer was separated and dried over calcium chloride. Bromobenzene was distilled off, and the residue was vacuum-distilled. A second distillation yielded 61 g (76%) of a substance having b.p. 117.5-118° (5 mm), n_D^{20} 1.5830; and d_4^{20} 1.5532.

Found: MR 57.23

$C_9H_7BrCl_2\overline{|}_4$. Calculated: MR 57.19

Found%: C 40.59; 40.61, H 2.71; 2.73;
Halogen 56.76; 56.77

$C_9H_7Cl_2Br$. Calculated%: C 40.64; H 2.65; Halogen 56.71

Hydrolysis of 3-p-Bromophenyl-1,1-dichloropropene to p-Bromohydrocinnamic Acid. A vigorously stirred mixture of the product of the previous experiment (20 g) and 93% sulfuric acid (50 g) was heated at 120° for one hour. The reaction mixture was cooled and poured into water, and the acid that separated was filtered off, washed, and dried. The yield of crude acid was 16.7 g (93%). The acid, recrystallized from heptane, melted at 135°. For p-bromohydrocinnamic acid the literature [2] gives m.p. 136°.

Found %: C 47.50; 47.81, H 4.15; 4.09;
H3.96; Br 34.88

$C_9H_9O_2Br$. Calculated%: C 47.18; Br 34.54; 34.50

Dehydration of 6 g of the crude acid with concentrated sulfuric acid at 145° yielded 3.5 g (63%) of 6-bromo-1-indanone, melting at 111-112° after crystallization from aqueous alcohol. For 6-bromo-1-indanone the literature [3] gives m.p. 111-112°.

Found%: C 51.25; 51.03; H 3.50; 3.47; Br 37.51;
37.66

C_9H_7OBr. Calculated%: C 51.21; H 3.34; Br 37.86

Addition of Chlorine to 3-p-Bromophenyl-1,1-dichloropropene (Preparation of 3-p-Bromophenyl-1,1,1,2-tetrachloropropane). A strong current of chlorine was passed for six hours through 40 g (0.15 mole) of 3-p-bromophenyl-1,1-dichloropropene at 60°, and the resulting increase in weight was 9.6 g (0.13 mole). The reaction mixture was cooled and a crystalline precipitate formed, which was separated and crystallized three times from ethanol. The product, amounting to 32 g (65%), melted at 89°.

Found %: C 31.58; 31.53; H 2.16 2.13; Halogen 65.95; 65.7

$C_9H_7Cl_4Br$. Calculated%: C 32.08; H 2.10; Halogen 65.82

Condensation of Chlorobenzene with 3,3,3-Trichloropropene (Preparation of 1,1-Dichloro-3-p-chlorophenylpropene. Reaction between 45 g (0.31 mole) of 3,3,3-trichloropropene and 180 g of chlorobenzene in presence of 1 g of aluminum chloride proceeded with evolution of heat, and in order to carry it out smoothly it was necessary to cool the reaction mixture. Reaction was complete in 5-10 minutes, and the calculated amount of hydrogen chloride was evolved. The reaction product was isolated as in the experiment with bromobenzene, and 51.2 g (74.5%), b.p. 115-116° (6 mm), was obtained in addition to 11 g of residue. The isolated compound had n_D^{20} 1.5630 and d_4^{20} 1.3208.

Found MR 54.47

$C_9H_7Cl_3\overline{|}_4$. Calculated MR 54.30

Found%; C 48.71; 48.94; H 3.24; 3.34; Cl 47.60; 48.04

$C_9H_7Cl_3$. Calculated%: C 48.79; H 3.19; Cl 48.02

Hydrolysis of 1,1-Dichloro-3,p-chlorophenylpropene to p-Chlorohydrocinnamic Acid. A vigorously stirred mixture of the product of the previous experiment (18 g) and 93% sulfuric acid (60 g) was heated at 110° for 45 minutes. The reaction mixture was cooled and poured onto ice, and the acid that separated was filtered off, washed and dried. The yield of crude product was 12.3 g (82%). Recrystallization from aqueous alcohol and from heptane yielded a substance melting at 122.5-123°. For p-chlorohydrocinnamic acid the literature [4] gives m.p. 123°.

Found %: C 58.55; 58.38; H 5.06; 5.01
$C_9H_9O_2Cl$. Calculated %: C 58.55; H 4.91

A sample of the acid was heated with twelve times its weight of concentrated sulfuric acid at 180°, and 6-chloro-1-indanone, m.p. 79-80° (from alcohol), was obtained. For 6-chloro-1-indanone the literature [4] gives m.p. 79-80°.

Addition of Chlorine to 1,1-Dichloro-3-p-chlorophenylpropene (Preparation of 1,1,1,2-Tetrachloro-3 p-chlorophenylpropane. Chlorine was passed through 79 g of 1,1-dichloro-3-p-chlorophenylpropene, the temperature of the mixture being maintained at 30° by cooling. When an increase in weight of 25 g had been attained (two hours), the reaction mixture was cooled, and the crystalline precipitate was separated. Distillation at 142-143° (5 mm) yielded 81 g (78%) of product, which melted at 90° after repeated recrystallization from ethanol.

Found %: C 37.14; 37.34; H 2.87; 2.85; Cl 61.04; 61.04
$C_9H_7Cl_5$. Calculated %: 36.96; H 2.41; Cl 60.63

Condensation of Anisole with 3,3,3-Trichloropropene (Preparation of 1,1-Dichloro-3-p-methoxyphenylpropene. A mixture of 44 g (0.30 mole) of 3,3,3-trichloropropene, 93 g (0.86 mole) of anisole, and 2 g of aluminum chloride was heated at 90° for three hours. In the course of the reaction a further 5 g of aluminum chloride was added. When reaction was complete the cooled mixture was diluted with water and extracted with chloroform. The extract was dried over calcium chloride. Solvent and excess of anisole were distilled off, and the residue was vacuum-distilled. Redistillation gave 48 g (74%) of a fraction having b.p. 118-119° (5 mm), n_D^{20} 1.5486 and d_4^{20} 1.2307;

Found MR 56.06
$C_{10}H_{10}OCl_2\overline{F}_4$. Calculated MR 55.69
Found %: C 55.34; 55.54; H 4.74; 4.75; Cl 32.69; 32.54
$C_{10}H_{10}OCl_2$. Calculated %: C 55.32; H 4.61; Cl 32.67

Oxidation of the product with a 5% alkaline solution of potassium permanganate gave a 90% yield of p-anisic acid, m.p. 184.5°.

Found %: C 63.42; 63.56; H 5.39; 5.41
$C_8H_8O_3$. Calculated %: C 63.15; H 5.30

For p-anisic acid the literature [5] gives m.p. 184.5°.

Condensation of Phenol with 3,3,3-Trichloropropene. A mixture of 66 g (0.45 mole) of 3,3,3-trichloropropene 220 g (2.34 moles) of freshly distilled phenol, and 4 g of aluminum chloride was heated in a boiling water bath for four hours. The mixture was cooled, diluted with water, and extracted with chloroform. The chloroform extract was dried over calcium chloride. After solvent and unchanged original substances had been distilled off, 75 g of a substance distilling over the range 100-160° (5 mm) was obtained, together with 8 g of residue. Fractionation through a 40-cm column gave a fraction, amounting to 48 g (50%), having b.p. 116-117° (3 mm), n_D^{20} 1.5727; and d_4^{20} 1.3050.

Found MR 51.25
$C_9H_8OCl_2\overline{F}_4$. Calculated MR 51.00
Found %: C 53.41; 53.29; H 4.10; 4.04; Cl 34.37; 34.38
$C_9H_8OCl_2$. Calculated %: C 53.23; H 3.97; Cl 34.92

A second fraction, amounting to 21 g (22%), had b.p. 130-131° (3 mm), n_D^{20} 1.5732 and d_4^{20} 1.3057.

Found MR 51.26
$C_9H_8OCl_2\overline{F}_4$. Calculated MR 51.00
Found %: C 53.44; 53.64; H 4.01; 4.01; Cl 34.89; 34.55
$C_9H_8Cl_2O$. Calculated %: C 53.23; H 3.97; Cl 34.92

When allowed to stand, the substance solidified: m.p. 40.5-41° (from petroleum ether).

The lower-boiling compound was o-(3,3-dichloroallyl)phenol, and the higher-boiling compound was the corresponding p-substituted phenol.

When the reaction between phenol and 3,3,3-trichloropropene was carried out in absence of aluminum chloride, but otherwise under the same conditions, the same products were obtained, but the total yield was only 50%.

Methylation of the Products of the Condensation of Phenol with 3,3,3-Trichloropropene. The substance boiling at 116° (3 mm) obtained in the previous experiment was methylated with the equivalent amount of dimethyl sulfate, and a compound having b.p. 109° (4.5 mm), n_D^{20} 1.5525 and d_4^{20} 1.2372, was obtained in almost quantitative yield.

Found MR 56.13

$C_{10}H_{10}OCl_2F_4$. Calculated MR 55.69

Found %: C 55.13; 55.02; H 4.69; 4.50; Cl 32.57; 32.18

$C_{10}H_{10}OCl_2$. Calculated %: C 55.32 H 4.61; Cl 32.67

Oxidation of this compound with alkaline potassium permanganate gave an 85% yield of o-anisic acid, m.p. 93.5°.

Found %: C 63.08; 63.00; H 5.27; 5.44

$C_8H_8O_3$. Calculated %: C 63.15; H 5.30

For o-anisic acid the literature [6] gives m.p. 98.5°.

Methylation of the second isomer, b.p. 130° (3 mm), yielded a methoxy compound identical in its constants with the 1,1-dichloro-3-p-methoxyphenylpropene obtained by the condensation of anisole with 3,3,3-trichloropropene. A mixture melting point test on the anisic acids obtained from the two samples of dichloro(methoxyphenyl) propene showed no depression.

Reaction of Sodium Phenoxide with 3,3,3-Trichloropropene. A solution of 1 mole of phenol, 1 mole of caustic soda, and 0.25 mole of 3,3,3-trichloropropene in 100 ml of ethanol was heated in a boiling water bath for six hours. The reaction mixture was diluted with water, and excess of aqueous caustic soda was added. The mixture was extracted with ether, and the ether extract was dried over calcium chloride. Solvent was distilled off, and the residue yielded 12 g of a neutral substance, probably consisting of 1,1-dichloro-3-phenoxypropene, b.p. 103-104° (7 mm); n_D^{20} 1.5534; d_4^{20} 1.2718.

Found %: C 52.90; 53.07; H 3.69; 3.79; Cl 34.85

Calculated %: C 53.23; H 3.97; Cl 34.92

Found MR 51.13

$C_9H_8OCl_2F_4$. Calculated MR 51.12

Acidification of the alkaline solution yielded 16 g of an oil, which was found to be a mixture of two isomers of (3,3-dichloroallyl)phenol.

Hydrolysis of 1,1-Dichloro-3-p-methoxyphenylpropene. A mixture of 10 g of p-$CH_3OC_6H_4CH_2CH = CCl_2$ and 30 g of 90% sulfuric acid was heated at 100-110° until hydrogen chloride ceased to be evolved (20 minutes). The reaction mixture was poured into water and treated with excess of barium carbonate. The precipitate of barium sulfate was filtered off, and the mother liquor was evaporated until crystallization began, when precipitation was effected by addition of alcohol. The barium sulfonate that separated was purified by reprecipitation from water with alcohol and was then dried over phosphoric oxide in a vacuum. The yield was about 90%.

Found %: C 36.16; 36.98; H 3.53; 3.41; S 9.70; 9.86

$Ba[SO_3C_6H_3(OCH_3)CH_2CH_2COOH]_2$ Calculated % C 36.62; H 3.38; S 9.78

Hydrolysis of 1,1-Dichloro-3-phenylpropene. The hydrolysis of 52 g of $C_6H_5CH_2CH = CCl_2$ was effected with 180 g of 92% sulfuric acid at 55-60° for 20-30 minutes. When the reaction mixture was set aside in the cold overnight, crystals of free sulfonic acid were precipitated in 95% yield. The pure sulfohydrocinnamic acid was obtained by passing an aqueous solution of its barium salt through a cationite and then evaporating the solution and vacuum-drying the product in a Fischer pistol heated by methanol vapor. The product formed colorless hygroscopic crystals that rapidly darkened.

Found %: C 43.09; 43.18; H 4.77; 4.71; S 12.62 12.55

$C_6H_4(SO_3H)CH_2CH_2CO_2H \cdot H_2O$. Calculated %: C 43.54; H 4.87; S 12.92

SUMMARY

1. A study was made of the condensation of 3,3,3-trichloropropene with bromobenzene, chlorobenzene, and anisole, and the following previously unknown compounds were isolated in the pure state: $p\text{-}BrC_6H_4CH_2CH=CCl_2$; $p\text{-}ClC_6H_4CH_2CH=CCl_2$; $p\text{-}CH_3OC_6H_4CH_2CH=CCl_2$.

2. It was found that, when 3,3,3-trichloropropene reacts with phenol in presence or absence of aluminum chloride, a mixture of $HOC_6H_4CH_2CH=CCl_2$ and $p\text{-}HOC_6H_4CH_2CH=CCl_2$ is formed. When the condensation is carried out with sodium phenoxide in an alcoholic medium, not only the above-mentioned ortho and para isomers are formed, but also the phenoxy derivative $C_6H_5OCH_2CH=CCl_2$.

3. It was shown that 1,1-dichloro-3-p-chlorophenylpropene and 3-p-bromophenyl-1,1-dichloropropene unite with chlorine with formation of $p\text{-}ClC_6H_4CH_2CHCl\cdot CCl_3$ and $p\text{-}BrC_6H_4CH_2CHClCCl_3$.

4. A study was made of the hydrolysis of the following compounds by concentrated H_2SO_4: $p\text{-}ClC_6H_4CH_2CH=CCl_2$; $p\text{-}BrC_6H_4CH_2CH=CCl_2$; $p\text{-}CH_3OC_6H_4CCH_2H=CCl_2$ and $C_6H_5CH_2CH=CCl_2$. It was found that the first two compounds are converted smoothly into the corresponding halohydrocinnamic acids; the other two compounds are not only hydrolyzed at the dichlorovinyl group, but are also sulfonated in the benzene ring.

LITERATURE CITED

[1] A. N. Nesmeyanov, R. Kh. Freidlina, and V. I. Firstov, Bull. Acad. Sci., USSR, Div. Chem. Sci., 1951, No. 5, 505.

[2] S. Gabriel, J. Zimmermann, Ber. 13, 1683 (1880).

[3] W. Miller, Rohde, Ber. 23, 1891 (1890).

[4] W. Miersch, Ber. 25, 2112 (1892).

[5] J. F. Eykman, Ber. 22, 2744 (1889).

[6] C. Grabe, Ann. 139, 139 (1866).

Received December 29, 1954

Institute of Heteroorganic Compounds
of the USSR Academy of Sciences

DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 12. DIESTERS OF 2-(2-ALKOXYETHOXY)VINYLPHOSPHONO-MONO-, DI-, AND -TRI-THIOIC ACIDS

K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov

This paper describes the preparation and some of the properties of diester of 2-(2-alkoxyethoxy)vinylphosphono-mono-, -di-, and -tri-thioic acids. The information in the literature on such esters is very limited. We have found a simple and readily accessible method for the synthesis of 2-alkoxy- and 2-phenoxy-vinylphosphonothioic dichlorides and 2-(2-alkoxyethoxy)vinylphosphonothioic dichlorides by the action of hydrogen sulfide on the product of the addition of phosphorus pentachloride to a vinyl ether [1].

The phosphonothioic dichlorides being readily accessible, we decided to prepare derivatives of these (esters and thio esters) by the reactions:

$$ROCH_2-CH_2-O-CH=CHPOCl_2 + 2NaSR = ROCH_2-CH_2-O-CH=CHPO(SR)_2 + 2NaCl. \quad (1)$$

$$ROCH_2-CH_2-O-CH=CHPSCl_2 + 2NaOR = ROCH_2-CH_2-O-CH=CHPS(OR)_2 + 2NaCl. \quad (2)$$

$$ROCH_2-CH_2-O-CH=CHPSCl_2 + 2NaSR = ROCH_2-CH_2-O-CH=CHPS(SR)_2 + 2NaCl. \quad (3)$$

In this way we prepared S,S-diethyl 2-(2-methoxyethoxy)- and 2-(2-butoxyethoxy)-vinylphosphonodithioates, O,O-dimethyl and O,O-diethyl 2-(2-methoxyethoxy)-, 2-(2-ethoxyethoxy)- and 2-(2-butoxyethoxy)-vinylphosphonothioates, and diethyl 2-(2-methoxyethoxy)- and 2-(2-ethoxyethoxy)-vinylphosphonotrithioates. The constants of these compounds are given in the table.

Diesters of 2-(2-alkoxyethoxy)vinylphosphono-mono-, -di-, and -tri-thioic acids are liquids of somewhat unpleasant odor, soluble in all organic solvents, and distillable only under reduced pressure.

EXPERIMENTAL

O,O-Dimethyl 2-(2-Methoxyethoxy)vinylphosphonothioate $CH_3OCH_2CH_2OCH=CHPS(OCH_3)_2$. Sodium methoxide was prepared in a three-necked flask fitted with stirrer and reflux condenser from 40 ml of absolute methanol and 2.3 g of sodium, and it was stirred and cooled with ice water while 10.85 g of 2-(2-methoxyethoxy)vinylphosphonothioic dichloride was added gradually. The reaction mixture was then diluted with 100 ml of absolute ether and set aside overnight. On the next day the mixture was heated for two hours in a water bath at 35° ; the ether layer was then removed, and the precipitate present was washed several times with ether. Vacuum fractionation gave a product amounting to 6.5 g (58%), having b.p. 119° (2 mm); n_D^{20} 1.4775; d_4^{20} 1.1624.

Found %: P 13.64; 13.63

$C_7H_{15}O_4PS$. Calculated %: P 13.71

O,O-Diethyl 2-(2-Methoxyethoxy)vinylphosphonothioate $CH_3OCH_2CH_2OCH=CHPS(OC_2H_5)_2$. 2-(2-Methoxyethoxy)vinylphosphonothioic dichloride (11.85 g) was added with cooling and slow stirring to sodium ethoxide, prepared from 2.3 g of sodium and 60 ml of absolute ethanol. When reaction was complete, the mixture was diluted with 120 ml of absolute ether and set aside overnight. On the next day the mixture was warmed in a water bath and the ether layer was poured off, the precipitate being washed several times with ether. Drying over sodium sulfate, followed by vacuum fractionation, yielded 10 g (73.5%) of a substance having b.p. 120° (1 mm); n_D^{20} 1.4760; d_4^{20} 1.0904.

Found %: P 12.19; 12.13

$C_9H_{19}H_4PS$. Calculated %: P 12.20

O,O-Dimethyl 2-(2-Ethoxyethoxy)vinylphosphonothioate $C_2H_5OCH_2CH_2OCH=CHPS(OCH_3)_2$. 2-(2-Ethoxyethoxy)vinylphosphonothioic dichloride (12.45 g) was added gradually with cooling and stirring to sodium methoxide prepared

TABLE

Formula	B.p. °C (p in mm)	n_D^{20}	d_4^{20}	Yield (%)
$CH_3-O-CH_2-CH_2-O-CH=CHPO(SC_2H_5)_2$	150/1	1.5511	1.1435	80
$n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO(SC_2H_5)_2$	186/2	1.5365	1.1180	87
$CH_3-O-CH_2-CH_2-O-CH=CHPS(OCH_3)_2$	119/6	1.4775	1.1524	58
$CH_3-O-CH_2-CH_2-O-CH=CHPS(OC_2H_5)_2$	120/1	1.4760	1.0904	73
$C_2H_5-O-CH_2-CH_2-O-CH=CHPS(OCH_3)_2$	127/2	1.4712	1.1321	78
$C_2H_5-O-CH_2-CH_2-O-CH=CHPS(OC_2H_5)_2$	133/2	1.4695	1.0781	82
$n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPS(OCH_3)_2$	141/1	1.4690	1.0922	83
$n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPS(OC_2H_5)_2$	145/1	1.4680	1.0296	80
$CH_3-O-CH_2-CH_2-O-CH=CHPS(SC_2H_5)_2$	157/2	1.5890	1.1579	75
$C_2H_5-O-CH_2-CH_2-O-CH=CHPS(SC_2H_5)_2$	176/2	1.5745	1.1417	83

from 2.3 g of sodium and 50 ml of absolute methanol. When the addition was complete, the mixture was diluted with 100 ml of ether. On the next day treatment as described above yielded 9.7 g (78%) of a substance having b.p. 127° (2 mm); n_D^{20} 1.4712; d_4^{20} 1.1321.

Found %: P 12.95; 12.84

$C_8H_{17}O_4PS$. Calculated %: P 12.84

O,O-Diethyl 2-(2-Ethoxyethoxy)vinylphosphonothioate $C_2H_5OCH_2CH_2OCH=CHPS(OC_2H_5)_2$. 2-(2-Ethoxyethoxy)vinylphosphonothioic dichloride (12.45 g) was added gradually with cooling and stirring to sodium ethoxide prepared from 2.3 g of sodium and 50 ml of absolute ethanol. When the addition was complete, the reaction mixture was diluted with 100 ml of ether and set aside overnight. On the next day the ether layer was poured off and the precipitate was washed several times with ether. Fractional distillation under reduced pressure yielded 11.4 g (82%) of a substance having b.p. 133° (2 mm); n_D^{20} 1.4695; d_4^{20} 1.0781.

Found %: P 10.15; 10.14

$C_{10}H_{21}O_4PS$. Calculated %: P 10.10

O,O-Dimethyl 2-(2-Butoxyethoxy)vinylphosphonothioate $n\text{-}C_4H_9OCH_2CH_2OCH=CHPS(OCH_3)_2$. 2-(2-Butoxyethoxy)vinylphosphonothioic dichloride (8g) was added gradually with stirring and cooling to sodium methoxide prepared from 50 ml of absolute methanol and 1.3 g of sodium. When reaction was complete, the mixture was diluted with 110 ml of absolute ether. On the next day the mixture was warmed in a water bath for two hours, the ether layer was poured off, and the precipitate was washed repeatedly with ether. The ether solution of the reaction mixture was dried over sodium sulfate. Fractionation then gave 6.5 g (83%) of a substance with b.p. 141° (1 mm); n_D^{20} 1.4690; d_4^{20} 1.0922.

Found %: P 10.77; 10.95

$C_{10}H_{21}O_4P$. Calculated %: P 11.19

O,O-Diethyl 2-(2-Butoxyethoxy)vinylphosphonothioate $n\text{-}C_4H_9OCH_2CH_2OCH=CHPS(OC_2H_5)_2$. 2-(2-Butoxyethoxy) vinylphosphonothioic dichloride (18.9 g) was added with stirring to sodium ethoxide prepared from 60 ml of absolute ethanol and 2.3 g of sodium. When the addition was complete, the mixture was diluted with 120 ml of absolute ether. On the next day the above-described operations yielded 17 g (80%) of a substance having b.p. 145° (1 mm) n_D^{20} 1.4680; d_4^{20} 1.0296.

Found %: P 10.51; 10.32

$C_{12}H_{25}O_4PS$. Calculated %: P 10.47

S,S-Diethyl 2-(2-Methoxyethoxy)vinylphosphonodithioate $CH_3OCH_2CH_2OCH=CHPO(SC_2H_5)_2$. Sodium (2.3 g), finely dispersed for reaction by the Brühl method, was added to absolute ether contained in a three-necked flask fitted with stirrer and reflux condenser. The mixture was cooled with ice and salt and was stirred slowly while dropwise addition of 8 g of ethanethiol was made. On the next day the resulting sodium mercaptide was warmed in a water bath 35°, and was then cooled again and stirred while 10.95 g of 2-(2-methoxyethoxy)vinylphosphonic dichloride was added. The mixture was then left overnight. On the next day it was heated in a water bath at 35° for 2 hours 30 minutes, the ether layer was poured off, and the precipitate was repeatedly washed with ether. The ethereal filtrate, dried over sodium sulfate and fractionated, yielded 10 g (80%) of a substance having b.p. 150° (1 mm); n_D^{20} 1.5511; d_4^{20} 1.1435.

Found %: P 11.49; 11.40

$C_9H_{19}O_3PS_2$. Calculated %: P 11.48

S,S-Diethyl 2-(2-Butoxyethoxy)vinylphosphonodithioate $n\text{-}C_4H_9OCH_2CH_2OCH=CHPO(SC_2H_5)_2$. 2-(2-Butoxyethoxy)vinylphosphonic dichloride (12 g) was added gradually with stirring to sodium ethylmercaptide prepared in absolute ether from 2.3 g of finely dispersed sodium and 8 g of ethanethiol. The product, amounting to 12.5 g (87%), had b. p. 186° (2 mm); n_D^{20} 1.5365; d_4^{20} 1.1180.

Found %: P 9.82; 9.91
$C_{12}H_{25}O_3PS_2$. Calculated %: P 9.93

Diethyl 2-(2-Methoxyethoxy) vinylphosphonotrithioate $CH_3OCH_2CH_2OCH = CHPS(SC_2H_5)_2$. Ethanethiol (9 g) was added gradually with stirring to an ice-cooled mixture of 2.3 g of Brühl sodium and absolute ether contained in a three-necked flask fitted with stirrer. On the next day 11.75 g of 2-(2-methoxyethoxy) vinylphosphonothioic dichloride was added with stirring to the sodium ethylmercaptide. Treatment of the reaction mixture in the way described above yielded 11 g (75%) of a substance having b. p. 157° (2 mm); n_D^{20} 1.5890; d_4^{20} 1.1579.

Found %: P 10.87; 10.88
$C_9H_{19}O_2PS_3$ Calculated %: P 10.83

Diethyl 2-(2-Ethoxyethoxy) vinylphosphonotrithioate $C_2H_5OCH_2CH_2OCH = CHPS(SH_2H_5)_2$. 2-(2-Ethoxlyethoxy)vinylphosphonothioic dichloride (12.45 g) was added gradually to sodium mercaptide prepared from 9 g of ethanethiol and 2.3 g of finely dispersed sodium in a medium of absolute ether. On the next day the mixture was warmed for two hours in a water bath at 35°, the ether layer was poured off, and the precipitate was washed repeatedly with ether. The ether filtrate, dried over sodium sulfate and fractionated, yielded 12.5 g (83%) of a substance having b. p. 176° (1 mm); n_D^{20} 1.5745; d_4^{20} 1.1417.

Found %: P 10.44; 10.46
$C_{10}H_{21}O_2P_3$. Calculated %: P 10.33

SUMMARY

1. Reaction of 2-(2-alkoxyethoxy) vinylphosphonothioic dichlorides with sodium methoxide and ethoxide yielded 0.0-dimethyl and 0.0-diethyl esters of 2-(2-methoxyethoxy)-, 2-(2-ethoxyethoxy)- and 2-(2-butoxyethoxy)-vinylphosphonothioic acids.

2. Reaction of 2-(2-alkoxyethoxy)vinylphosphonic and 2-(2-alkoxyethoxy)vinylphosphonothioic dichlorides with sodium ethylmercaptide yielded S,S-diethyl 2-(2-methoxyethoxy)- and 2-(2-butoxyethoxy)-vinylphosphonothioates and diethyl 2-(2-methoxyethoxy)- and 2-(2-ethoxyethoxy)-vinylphosphonotrithioates.

LITERATURE CITED

[1] K. N. Anisimov, N. E. Kolobova and A. N. Nesmeyanov, Bull. Acad. Sci., USSR, Div. Chem. Sci., 1954, No. 9, 799 (T. p. 689) *.

Received June 11, 1954

Institute of Heteroorganic Compounds
of the USSR Academy of Sciences

---

* T. p. = C. B. Translation pagination.

DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 14. DIESTERS OF STYRYLPHOSPHONIC ACID

K. N. Anisimov and A. N. Nesmeyanov

We have previously described diesters of 2-alkoxy- and 2-phenoxy-vinylphosphonic acids [1-3]. In the present paper we report the synthesis and some of the properties of diesters of styrylphosphonic acid (i.e. 2-phenylvinylphosphonic acid). The syntheses of these compounds were effected by the action of alcohols on styrylphosphonic dichloride, which we were the first to prepare and characterize [4]. Dimethyl styrylphosphonate is a white crystalline substance (m.p. 41-42°), soluble in many organic solvents and in water. The other esters are clear oily liquids of characteristic odor, soluble in the usual organic solvents, but not in water. The properties of the compounds obtained are given in the table.

EXPERIMENTAL

Dimethyl Styrylphosphonate $C_6H_5OCH = CHPO(OCH_3)_2$. A mixture of 3.2 g of absolute methanol, 7.9 g of pyridine, and 40 ml of dry benzene was prepared in a three-necked flask fitted with stirrer, reflux condenser protected with a calcium chloride tube, and a dropping funnel. With good cooling and stirring, a solution of 11.05 g of styrylphosphonic dichloride in 15 ml of benzene was added. When the whole of the acid chloride had been added, the reaction mixture was heated for two hours in a water bath, after which pyridine hydrochloride was filtered off and the filtrate was washed with saturated sodium carbonate solution and dried over calcined sodium sulfate. On the next day benzene was distilled from the filtrate and the residue was vacuum-distilled. Three fractionations yielded 6 g (57%) of dimethyl styrylphosphonate, b.p. 129° (2 mm), m.p. 41-42°.

Found %: C 56.42; 53.57; H 6.10; 6.20
$C_{10}H_{13}O_3P$. Calculated %: C 56.60; H 6.13

All of the following styrylphosphonic esters were synthesized by the method described for the dimethyl ester.

Diethyl Styrylphosphonate $C_6H_5OCH = CHPO(OC_2H_5)_2$. Styrylphosphonic dichloride (11.05 g) was added to 4.6 g of ethanol and 7.9 g of pyridine, and the product was 8 g (67%) of diethyl styrylphosphonate, b.p. 138° (2 mm) d_4^{20} 1.1082; n_D^{20} 1.5325.

Found %: C 60.11; 60.09; H 7.25; 7.28
$C_{12}H_{17}O_3P$. Calculated %: C 60.00; H 7.08

Dipropyl Styrylphosphonate $C_6H_5CH = CHPO(OC_3H_7\text{-}n)_2$. Styrylphosphonic dichloride (11.05 g) was added to 6 g of propyl alcohol and 7.9 g of pyridine, and the product was 10 g (75%) of dipropyl styrylphosphonate, b.p. 158° (2 mm); d_4^{20} 1.0700; n_D^{20} 1.5230.

Found %: C 62.82; 62.98; H 8.08; 8.11
$C_{14}H_{21}O_3P$. Calculated %: C 62.67; H 7.83

Diisopropyl Styrylphosphonate $C_6H_5CH = CHPO(OC_3H_7\text{-}i)_2$. With respect to the conditions and the amounts of the reactants, the procedure was precisely analogous to that used for the dipropyl ester. The product was 3.5 g (26%) of diisopropyl styrylphosphonate, b.p. 137° (1 mm); d_4^{20} 1.0547; n_D^{20} 1.5164.

Found %: C 62.81; 63.03; H 7.90; 7.78
$C_{14}H_{21}O_3P$. Calculated %: C 62.67; H 7.83

Dibutyl Styrylphosphonate $C_6H_5CH = CHPO(OC_4H_9\text{-}n)_2$. Styrylphosphonic dichloride (11.05 g) was added to 7.4 g of butyl alcohol and 7.9 g of pyridine, and the product was 12 g (81%) of a substance having b.p. 172° (2 mm);

TABLE

Formula	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}
$C_6H_5-CH=CHPO(OCH_3)_2$	129 (2), 41 - 42		
$C_6H_5-CH=CHPO(OC_2H_5)_2$	136 (2)	1.5326	1.1082
$C_6H_5-CH=CHPO(OC_3H_7\text{-}n)_2$	158 (2)	1.5230	1.0700
$C_6H_5-CH=CHPO(OC_3H_7\text{-}i)_2$	137 (1)	1.5164	1.0547
$C_6H_5-CH=CHPO(OC_4H_9\text{-}n)_2$	172−173 (2)	1.5153	1.0403
$C_6H_5-CH=CHPO(OC_4H_9\text{-}i)_2$	159 (2)	1.5130	1.0342
$C_6H_5-CH=CHPO(OC_3H_5)_2$	159 (2)	1.5445	1.1076
$C_6H_5-CH=CHPO(OC_6H_{13}\text{-}n)_2$	187.5 (2)	1.5500	1.0054
$C_6H_5-CH=CHPO(OC_7H_{15}\text{-}n)_2$	213 (2)	1.5020	0.9888
$C_6H_5-CH=CHPO(OCH_2-CH_2-O-CH_3)_2$	176 (2)	1.5246	1.1501
$C_6H_5-CH=CHPO(OCH_2-CH_2-O-C_2H_5)_2$	187 (2)	1.5179	1.1114

d_4^{20} 1.0403; n_D^{20} 1.5153.

Found %. C 64.81; 64.78; H 8.52; 8.48

$C_{16}H_{25}O_3P$. Calculated %: C 64.86; H 8.44

Diisobutyl Styrylphosphonate $C_6H_5CH=CHPO(OC_4H_9\text{-}i)_2$. This was prepared under the same conditions as those used for the dibutyl ester. The yield of diisobutyl styrylphosphonate was 10 g (67%), and it had b.p. 159° (2 mm) n_D^{20} 1.5130; d_4^{20} 1.0342.

Found %: C 64.47; 64.46; H 8.32; 8.28

$C_{16}H_{25}O_3P$. Calculated %: C 64.86; H 8.44

Diallyl Styrylphosphonate $C_6H_5CH=CHPO(OC_3H_5)_2$. Styrylphosphonic dichloride (22.1 g) was added to 11.62 g of allyl alcohol and 15.8 g of pyridine, and the product was 15 g (56%) of diallyl styrylphosphonate, b.p. 159° (2 mm) d_4^{20} 1.1076; n_D^{20} 1.5445.

Found %: C 63.53; 63.48; H 6.71; 3.50

$C_{14}H_{17}O_3P$. Calculated %: C 63.63; H 6.43

Dihexyl Styrylphosphonate $C_6H_5CH=CHPO(OC_6H_{13}\text{-}n)_2$. Styrylphosphonic dichloride (11.05 g) was added to 10.21 g of hexyl alcohol and 7.9 g of pyridine. The substance isolated had b.p. 187.5° (2 mm); d_4^{20} 1.0054; n_D^{20} 1.5500.

Found %: C 68.00; 68.12; H 9.71; 9.60

$C_{20}H_{33}O_3P$. Calculated %: C 68.18; H 9.37

Diheptyl Styrylphosphonate $C_6H_5-CH=CHPO(OC_7H_{15}\text{-}n)_2$. Styrylphosphonic dichloride (22.1 g) was added to 23.2 g of absolute heptyl alcohol and 15.8 g of pyridine. The substance isolated, amounting to 9.2 g (65%), had b.p. 213° (1 mm); n_D^{20} 1.5020; d_4^{20} 0.9888.

Found %: P 7.82; 7.93

$C_{22}H_{37}O_3P$ Calculated %: P 8.01

Bis(2-methoxyethyl)Styrylphosphonate $C_6H_5-CH=CHPO(OCH_2CH_2OCH_3)_2$. Styrylphosphonic dichloride (22.1 g) was added to 15.2 g of 2-methoxyethanol and 15.8 g of pyridine. The substance isolated (20 g) had b.p. 176° (2 mm); d_4^{20} 1.1501; n_D^{20} 1.5246.

Found %: P 10.38; 10.17

$C_{14}H_{21}O_5P$. Calculated %: P 10.33

Bis(2-ethoxyethyl) Styrylphosphonate $C_6H_5-CH=CHPO(OCH_2-CH_2-OC_2H_5)_2$. Styrylphosphonic dichloride (22.1 g) was added to 18 g of 2-ethoxyethanol and 15.8 g of pyridine. Fractionation yielded 21 g of ester, b.p. 187° (2 mm); d_4^{20} 1.1114; n_D^{20} 1.5179.

Found %: C 58.28; 58.17; H 7.63; 7.43

$C_{16}H_{25}O_5P$. Calculated %: C 58.53; H 7.62

SUMMARY

Eleven diesters of styrylphosphonic acid were prepared and characterized.

LITERATURE CITED

[1] K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov, Bull. Acad. Sci., USSR, Div. Chem. Sci., 1955, No. 2, 240 (T.p. 213) *.

[2] K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov, Bull. Acad. Sci., USSR, Div. Chem. Sci., 1955, No. 3, 425 (T.p. 377) *.

[3] K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov, Bull. Acad. Sci., USSR, Div. Chem. Sci., 1955, No. 3, 432 (T.p. 383) *.

[4] K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov, Bull. Acad. Sci., USSR, Div. Chem. Sci., 1954, No. 4, 610 (T.p. 521) *.

Received June 11, 1954

Institute of Heteroorganic Compounds
of the USSR Academy of Sciences

---

* T.p. = C. B. Translation pagination.

DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 15. DIESTERS OF β-CHLOROSTYRYLPHOSPHONIC AND PHENYLETHYNYLPHOSPHONIC ACIDS

K. N. Anisimov and A. N. Nesmeyanov

β-Chlorostyrylphosphonic dichloride reacts with alcohols in presence of pyridine in the same manner as all acid chlorides of unsaturated phosphonic acids [1], i.e. with formation of diesters of β-chlorostyrylphosphonic acid together with pyridine hydrochloride. By this method we have prepared the dimethyl, diethyl, dipropyl, diisopropyl, dibutyl, diisobutyl, and diallyl esters of β-chlorostyrylphosphonic acid.

Dimethyl β-chlorostyrylphosphonate has been prepared previously by Bergman and Bondi [2] by reaction between methyl iodide and silver β-chlorostyrylphosphonate; these authors report only the boiling point of the compound.

All of the esters synthesized are viscous liquids, soluble in organic solvents. They are stable to storage, with the exception of diisopropyl β-chlorostyrylphosphonate, and this decomposes partially when vacuum-distilled and polymerizes in the flask. All the other esters can be vacuum-distilled without decomposition. Physical constants of the compounds obtained are given in Table 1.

For dimethyl β-chlorostyrylphosphonate, Bergman and Bondi [2] give b.p. 202-203° (14 mm).

The values of the boiling points, densities, and refractive indices of diesters of β-chlorostyrylphosphonic acid are higher than those of the corresponding diesters of styrylphosphonic acid. When diethyl or diisobutyl β-chlorostyrylphosphonate was treated with the calculated amount of alcoholic potash in the cold, potassium chloride was precipitated, and the corresponding ester of phenylethynylphosphonic acid was formed. Diethyl and diisobutyl phenylethynylphosphonates are clear liquids, insoluble in water, but soluble in many organic solvents. Their physical constants are given in Table 2.

EXPERIMENTAL

Dimethyl β-Chlorostyrylphosphonate $C_6H_5CCl=CHPO(OCH_3)_2$. A mixture of 3.2 g of absolute methanol, 7.9 g of pyridine, and 50 ml of benzene was prepared in a three-necked flask fitted with stirrer, reflux condenser protected with a calcium chloride tube, and dropping funnel. With good cooling and stirring, dropwise addition was made of a solution of 12.77 g of β-chlorostyrylphosphonic dichloride in 15 ml of benzene. On the next day the reaction mixture was heated for two hours in a water bath. Pyridine hydrochloride was then filtered off, and the filtrate was washed three times with saturated sodium carbonate solution and dried over calcined sodium sulfate. On the next day benzene was distilled from the filtrate, and the residue was vacuum-distilled. Three fractionations yielded 6 g (48%) of dimethyl β-chlorostyrylphosphonate, b.p. 148-149° (1 mm); d_4^{20} 1.2812; n_D^{20} 1.5595.

Found %: C 49.04; 48.86; H 5.39; 5.34

$C_{10}H_{12}O_3PCl$. Calculated %: C 48.68; H 4.86

The other β-chlorostyrylphosphonic esters were synthesized by the method described above.

Diethyl β-Chlorostyrylphosphonate $C_6H_5CCl=CHPO(OC_2H_5)_2$. β-Chlorostyrylphosphonic dichloride (12.77 g) was added to 4.6 g of absolute ethanol and 7.9 g of pyridine. The product was 9 g (65%) of diethyl β-chlorostyrylphosphonate, b.p. 159° (2 mm); d_4^{20} 1.2070; n_D^{20} 1.5410.

Found %: C 52.52; 52.43; H 6.06; 5.95

$C_{12}H_{16}O_3ClP$. Calculated %: C 52.45; H 5.82

Diallyl β-Chlorostyrylphosphonate $C_6H_5CCl=CHPO(OC_3H_5)_2$. β-Chlorostyrylphosphonic dichloride (12.77 g) was added to 5.8 g of allyl alcohol and 7.9 g of pyridine. The product was 8 g (53%) of diallyl β-chlorostyrylphosphonate, b.p. 164-165° (1 mm); d_4^{20} 1.1920; n_D^{20} 1.5504.

Found %: C 56.00; 56.15; H 5.11; 5.17

$C_{14}H_{16}O_3ClP$. Calculated %: C 56.37; H 5.38

Dipropyl β-Chlorostyrylphosphonate $C_6H_5CCl = CHPO(OC_3H_7\text{-}n)_2$. β-Chlorostyrylphosphonic dichloride (12.77 g) was added gradually to 6 g of propyl alcohol. The reaction was carried out in presence of 8 g of pyridine in a benzene medium. The product was 10 g (60%) of dipropyl β-chlorostyrylphosphonate, b.p. 166° (2 mm); d_4^{20} 1.1584; n_D^{20} 1.5288.

Found %: C 55.29; 55.26; H 6.65; 6.72

$C_{14}H_{20}O_3ClP$. Calculated %: C 55.53; H 6.61

TABLE 1

Formula	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}
$C_6H_5CCl = CHPO(OCH_3)_2$	148–149 (1)	1.5595	1.2812
$C_6H_5CCl = CHPO(OC_2H_5)_2$	159 (2)	1.5410	1.2070
$C_6H_5-CCl = CHPO(OC_3H_7-n)_2$	166 (2)	1.5288	1.1584
$C_6H_5-CCl = CHPO(OC_3H_7-i)_2$	149 (1)	1.5220	1.1424
$C_6H_5-CCl = CHPO(OC_4H_9-n)_2$	176 (1)	1.5212	1.1202
$C_6H_5-CCl = CHPO(OC_4H_9-i)_2$	165 (1)	1.5188	1.1168
$C_6H_5-CCl = CHPO(OC_6H_5)_2$	164–165 (1)	1.5504	1.1920

TABLE 2

Formula	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}
$C_6H_5C \equiv CPO(OC_2H_5)_2$	155 (1)	1.5312	1.1500
$C_6H_5C \equiv CPO(OC_4H_9-i)_2$	159–161 (1)	1.5090	1.0423

Diisopropyl β-Chlorostyrylphosphonate $C_6H_5CCl = CHPO(OC_3H_7\text{-}i)_2$. To 5 g of isopropyl alcohol and 7.9 g of pyridine, 12.77 g of β-chlorostyrylphosphonic dichloride was added. The product was 3 g of diisopropyl β-chlorostyrylphosphonate, b.p. 149° (1 mm); d_4^{20} 1.1424; n_D^{20} 1.5220.

Found %: C 55.68; 55.78; H 6.65; 6.88

$C_{14}H_{20}O_3ClP$. Calculated %: C 55.53; H 6.61

Dibutyl β-Chlorostyrylphosphonate $C_6H_5CCl = CHPO(OC_4H_9-n)_2$. β-Chlorostyrylphosphonic dichloride (12.77 g) was added to 4.7 g of butyl alcohol. The reaction was carried out in presence of 7.9 g of pyridine in a benzene medium. The product was 12 g (81%) of dibutyl β-chlorostyrylphosphonate, b.p. 176° (1 mm); d_4^{20} 1.1202; n_D^{20} 1.5212

Found %: C 57.89; 58.18; H 7.40; 7.34

$C_{16}H_{24}O_3ClP$. Calculated %: C 58.09; H 7.26

Diisobutyl β-Chlorostyrylphosphonate $C_6H_5CCl = CHPO(OC_4H_9-i)_2$. This was prepared under the same conditions as those used for the preparation of the dibutyl ester. The yield of dissobutyl β-chlorostyrylphosphonate was 10 g (60%), and it had b.p. 165° (1 mm); d_4^{20} 1.1168; n_D^{20} 1.5188.

Found %: C 57.96; 57.80; H 7.24; 70.2

$C_{16}H_{24}O_3PCl$. Calculated %: C 58.09; H 7.26

Diethyl Phenylethynylphosphonate $C_6H_5C \equiv CPO(OC_2H_5)_2$ ethyl β-chlorostyrylphosphonate (3.82 g) was added to a solution of 0.77 g of caustic potash in alcohol. The solution immediately became warm, and potassium chloride was precipitated. The reaction mixture was heated for one hour in a water bath, and the precipitate was filtered off. Alcohol was distilled from the filtrate, and vacuum distillation of the residue yielded 2.6 g of a substance having b.p. 155° (1 mm); n_D^{20} 1.5312; d_4^{20} 1.1500.

Found %: P 13.00; 12.96

$C_{12}H_{15}O_3P$. Calculated %: P 13.02

Diisobutyl Phenylethynylphosphonate $C_6H_5C\equiv CPO(OC_4H_9\text{-}i)_2$. This was prepared similarly to the diethyl ester from 17.5 g of diisobutyl β-chlorostyrylphosphonate and 3.2 g of caustic potash. The product (10.8 g) had b.p. 159-161° (1 mm); n_D^{20} 1.5090; d_4^{20} 1.0423.

Found %: P 10.59; 10.57

$C_{16}H_{23}O_3P$. Calculated %: P 10.54

SUMMARY

1. The diethyl, dipropyl, diisopropyl, dibutyl, diisobutyl, and diallyl esters of β-chlorostyrylphosphonic acid were prepared and characterized for the first time.

2. The diethyl and diisobutyl esters of phenylethynylphosphonic acid were prepared and characterized.

LITERATURE CITED

[1] K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov, Bull. Acad. Sci., USSR, Div. Chem. Sci., 1955, No. 2, 240 (T.p. 213)*.

[2] E. Bergman, A. Bondi, Ber. 66, 278 (1933).

Received June 11, 1954

Institute of Heteroorganic Compounds
of the USSR Academy of Sciences

---

* T.p. = C.B. Translation pagination.

ACTION OF SODIUM ON COMPOUNDS CONTAINING A $CCl_2 = CH$ GROUP

L. I. Zakharkin

Pinner [1, 2] was the first to investigate the action of sodium on the 2,2-dichlorovinyl group, the compound selected for study being 1,1-dichloropropene. He showed that, when the product of reaction between 1,1-dichloropropene and sodium was decomposed with water, propyne was formed in low yield [2]; treatment of the reaction product with carbon dioxide gave propiolic acid [3]. Pinner supposed that, in the reaction of 1,1-dichloropropene with sodium, the product had the composition $C_3H_4Cl_2Na_2$, the course of the reaction being as follows, with separation of sodium chloride only during the stage of decomposition with water:

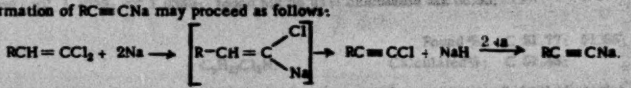
$$CH_3CH = CCl_2 + 2Na \rightarrow C_3H_4Cl_2Na_2 \xrightarrow{H_2O} CH_3C \equiv CH + 2NaCl.$$

This reaction has not been studied further.

Various 2,2-dichlorovinyl derivatives now being readily available [4, 5], we considered that it was of interest to investigate this reaction from the preparative point of view and also to elucidate the mechanism of the conversion of the $CCl_2 = CH$ group into the $HC \equiv C$ group, since we did not consider the mechanism postulated by Pinner to be very likely. We found, in agreement with previous work, that treatment of the product of reaction between 1,1-dichloro-1-pentene and sodium with carbon dioxide yielded 2-hexynoic acid, and that treatment of the product of reaction between 5,5-dichloro-N,N-diethyl-4-pentenylamine and sodium with benzaldehyde yielded 6-diethylamino-1-phenyl-2-hexyn-1-ol $C_6H_5CH(OH)C \equiv C-(CH_2)_3N(C_2H_5)_2$. These results show that the product of reaction between a 2,2-dichlorovinyl derivative and sodium contains $RC \equiv CNa$ and that this is formed by the removal of two chlorine atoms and one hydrogen atom from the $CCl_2 = CH$ group. It is to be expected that the chlorine will separate in the form of sodium chloride. It was found that only a very small amount of hydrogen was evolved in the reaction (2.5 % of the theoretical amount), and only when the reaction product was decomposed with water was the expected amount of hydrogen liberated (0.5 mole per mole of 2,2-dichlorovinyl derivative). It was found also that in this reaction it was necessary to take 4 g atoms of sodium for each mole of the 2,2-dichlorovinyl derivative, and not 2 g-atoms, as indicated by Pinner. These results can be explained on the assumption that hydrogen from the $CCl_2 = CH$ group becomes bound as sodium hydride, and the reaction of 2,2-dichlorovinyl derivative with sodium can be represented as follows:

$$RCH = CCl_2 + 4Na \rightarrow RC \equiv CNa + NaH + 2NaCl.$$

The formation of $RC \equiv CNa$ may proceed as follows:



$$RCH = CCl_2 + 2Na \longrightarrow \left[R-CH=C\begin{smallmatrix}Cl\\Na\end{smallmatrix}\right] \rightarrow RC \equiv CCl + NaH \xrightarrow{2\,Na} RC \equiv CNa.$$

Confirmation of this reaction mechanism can be found in the formation of some monosubstituted acetylene and sodium or lithium hydride, which was observed in a number of cases when monohalo olefins of the type $RCH = CHX$ were treated with sodium or lithium [6, 7]. The replacement of chlorine by sodium in $RC \equiv C-Cl$ occurs very readily [8]. Our study of the action of sodium on 2,2-dichlorovinyl derivatives showed that the reaction proceeds fairly smoothly: in most of the cases investigated it gave the monosubstituted acetylene in a yield of 60-80 %.

The properties and yields of the monosubstituted acetylenes obtained are given in Table 1. In the case of β,β-dichlorostyrene we did not succeed in obtaining a good yield of ethynylbenzene owing to the impossibility of carrying out the reaction to completion. In the case of (3,3-dichloroallyl)benzene the product, obtained in satisfactory yield, was a mixture of substances — mainly phenylpropadiene. Taking 4,5,5-trichloro-N,N-diethyl-4-pentenylamine as our example, we showed that the $CCl_2 = CCl$ group is converted by sodium into the $HC \equiv C$ group:

$$(C_2H_5)_2N(CH_2)_3CCl = CCl_2 + 4Na \rightarrow (C_2H_5)_2N(CH_2)_3C \equiv CNa + 3NaCl.$$

A good yield of N,N-diethyl-4-pentynylamine was obtained. Conversion of 5-ethoxy-1-pentyne into its organomagnesium bromide and treatment of the product with benzaldehyde gave a good yield of 6-ethoxy-1-phenyl-2-hexyn-1-ol.

EXPERIMENTAL

1,1-Dichloro-1-nonene. A mixture of 60 g of 1,1,1-trichlorononane and 3 g of anhydrous ferric chloride was heated at 60-75° until hydrogen chloride ceased to be evolved. The mixture was cooled, ferric chloride was filtered off, and the filtrate was diluted with chloroform and washed with hydrochloric acid. Fractionation through a column yielded 39.4 g (77.5%) of 1,1-dichloro-1-nonene, b.p. 85-86° (7 mm); n_D^{20} 1.4587; d_4^{20} 1.0106; found MR 52.84 Calculated MR 53.03.

Found %: C 55.21; 55.26; H 8.03; 8.11
$C_9H_{16}Cl_2$. Calculated %: C 55.38; H 8.20

1,1-Dichloro-5-ethoxy-1-pentene. A solution of 1-1-5-trichloro-1-pentene (40 g) and sodium ethoxide (from 6.5 g of sodium) in 85 ml of absolute alcohol was heated for four hours, cooled, and poured into water. The oil that separated was extracted with chloroform. Vacuum distillation yielded 29.3 g (69%) of 1,1-dichloro-5-ethoxy-1-pentene, b.p. 79-81° (11 mm); n_D^{20} 1.4642; d_4^{20} 1.1101; found MR 45.50; calculated MR 45 44.

Found %: C 46.02; 45.89; H 6.75; 6.72
$C_7H_{12}Cl_2O$. Calculated %: C 45.90; H 6.55

1,1-Dichloro-7-ethoxy-1-heptene. A solution of 1,1,7-trichloro-1-heptene (40 g) and sodium ethoxide (from 6 g of sodium) in 80 ml of absolute alcohol was heated for six hours. The product was 32.4 g (77%) of 1,1-dichloro-7-ethoxy-1-heptene, b.p. 114-116° (15 mm); n_D^{20} 1.4622; d_4^{20} 1.0603; found MR 54.71; calculated MR 54.68.

Found %: C 50.91; 51.04; H 7.45; 7.50
$C_9H_{16}Cl_2O$. Calculated %: C 51.23; H 7.58

1,1-Dichloro-9-ethoxy-1-nonene. This was prepared similarly to 1,1-dichloro-7-ethoxy-1-heptene in 73.5% yield. It had b.p. 88-89° (1 mm); n_D^{20} 1.4669; d_4^{20} 1.1054; found MR 63.81; calculated MR 64.00

Found %: C 55.45; 55.41 , H 8.21; 8.32
$C_{11}H_{20}Cl_2O$. Calculated %: C 55.23 H 8.36

5,5-Dichloro-N,N-diethyl-4-pentenylamine. A solution of 50 g of 1,1,5-trichloro-1-pentene and 50 g of diethylamine in 120 ml of methanol was heated in an autoclave at 100-115° for 5-6 hours. Excess of diethylamine and methanol was driven off from a water bath, and the residue was treated with hydrochloric acid. The undissolved oil was extracted with ether. The hydrochloric acid solution was rendered alkaline with cooling, and the oil that separated was extracted with ether. The product was 51.2 g (83.5%) of 5,5-dichloro-N,N-diethyl-4-pentenylamine, b.p. 63-64° (2 mm); n_D^{20} 1.4719; d_4^{20} 1.0349; found MR 56.81; calculated MR 56.93.

Found %: C 51.77; 51.55; H 8.29; 8.16
$C_9H_{17}Cl_2N$. Calculated %: C 51.43; H 8.09

7,7-Dichloro-N,N-diethyl-6-heptenylamine. This was prepared similarly to 5,5-dichloro-N,N-diethyl-4-pentenylamine in 88% yield. It had b.p. 89-90° (1.5 mm); n_D^{20} 1.4730; d_4^{20} 1.0097. Found MR 66.14; Calculated MR 66.21.

Found %: N 6.09; 6.18
$C_{11}H_{21}Cl_2N$. Calculated %: N 5.88

1,1-Dichloro-9-ethylthio-1-nonene. This was prepared by heating 1,1,9-trichloro-1-nonene with a small excess of C_2H_5SNa in alcoholic solution; the yield was 92.8%. It had b.p. 120-121° (1 mm); n_D^{20} 14991; d_4^{20} 1.0672. Found MR 70.17; Calculated MR 70.26.

Found %: C 51.62; 51.58; H 7.70; 7.88
$C_{11}H_{20}Cl_2S$. Calculated %: C 51.76; H 7.84

1,1-Dichloro-5-phenoxy-1-pentene. A solution of 1,1,5-trichloro-1-pentene (40 g), sodium iodide (1.5 g), and sodium phenoxide (from 28 g of phenol) in 100 ml of alcohol was heated for 8 hours 30 minutes. The product was 37. 6 g (70.5%) of 1,1-dichloro-5-phenoxy-1-pentene, b.p. 112-113° (2 mm); n_D^{20} 1.5375; d_4^{20} 1.1914.

TABLE 1

Formula of substance R—C ≡ CH	Yield (%)	B.p.-in °C (p in mm)	n_D^{18}	d_4^{20}	Molecular refraction		Found				Calculated	
					found	calculated	C		H		C	H
$n\text{-}C_5H_{11}C{\equiv}CH$	68	97—98	1.4120	—	—	—	—	—	—	—	—	—
$n\text{-}C_7H_{15}C{\equiv}CH$	71	148—150	1.4250	—	—	—	—	—	—	—	—	—
$C_2H_5O(CH_2)_3C{\equiv}CH$	72	126—127	1.4204	0.8268	34.31	34.17	74.77;	74.92	10.40;	10.86	75.00	10.71
$C_2H_5O(CH_2)_5C{\equiv}CH$	76	63—64 (10)	1.4289	0.8318	43.38	43.24	77.28;	77.37	11.52;	11.70	77.15	11.43
$C_2H_5O(CH_2)_7C{\equiv}CH$	76	94—95 (10)	1.4350	0.8336	52.59	52.64	78.51;	78.44	12.06;	12.09	78.57	11.90
$C_6H_5O(CH_2)_3C{\equiv}CH$	87	108—109 (9)	1.5210	0.9648	49.47	49.07	82.16;	82.22	7.91;	7.81	82.37	7.50
$(C_2H_5)_2N(CH_2)_3C{\equiv}CH$ a)	86	45—46 (8)	1.4410	0.8061	45.53	45.64	77.92;	77.70	12.14;	12.12	77.69	12.23
$(C_2H_5)_2N(CH_2)_5C{\equiv}CH$ b)	78	84—85 (10)	1.4460	0.8128	54.70	54.88						
$C_6H_5S(CH_2)_4C{\equiv}CH$ c)	90	129—130 (12)	1.4771	0.8854	58.73	58.92	71.27;	71.37	10.73;	10.87	71.73	10.87
$(C_2H_5O)_2CH{-}C{\equiv}CH$	75	118—120 (27)	1.4260	0.8752	54.08	54.22	71.78;	71.54	10.93;	11.02	71.73	10.87
$n\text{-}C_4H_9\underset{\substack{\mid\\OC_2H_5}}{C}H{-}C{\equiv}CH$	40	45—46 (9)	1.4206	0.8229	43.12	43.24	77.28;	77.32	11.54;	11.60	77.15	11.43

a) Oxalate, m.p. 105;106° (from alcohol) Found %: N 6.23; 6.35; Calculated %: N 6.39

b) Found %: N 8.44; 8.55; Calculated %: N 8.38; oxalate, m.p. 72;73° (from alcohol-ether)
Found %: N 5.52; 5.48; Calculated %: N 5.44.

c) Found %: S 17.30; 17.40; Calculated %: S 17.38.

Found %: C 57.04; 56.96; H 5.41; 5.30

$C_{11}H_{12}Cl_2O$. Calculated %: C 57.14; H 5.20

1,1,-Dichloro-3-ethoxy-1-heptene. An ethereal solution butylmagnesium bromide (from 30 g of butyl bromide and 5 g of magnesium was added gradually to a stirred ice-cooled solution of 37 g of 1,1,3-trichloro-3-ethoxypropene in 50 ml of dry ether. When the addition was complete, the mixture was stirred at room temperature for 30 minutes and poured into water (under cooling). The ether solution was washed with dilute hydrochloric acid and then with water; it was dried over potassium carbonate. Vacuum distillation yielded 31.2 g of 1,1-dichloro-3-ethoxy-1-heptene, b.p. 84-85° (9 mm); n_D^{20} 1.4530; d_4^{20} 1.0408; Found MR 54.79; Calculated MR 54.67.

Found %: C 51.01; 50.95; H 7.52; 7.66

$C_9H_{16}Cl_2O$. Calculated %: C 51.18; H 7.58

1,1-Dichloro-3,3-dibutoxypropene. This was prepared as already described [9].

Preparation of Acetylenes. A small amount of ethereal solution of the dichlorovinyl derivative was added to a stirred mixture of 0.38 g-atom of finely granulated sodium and 80-100 ml of dry ether, and the mixture was heated for a short time until reaction began. Heating was discontinued, and the remainder of the ethereal solution of the 2,2-dichlorovinyl derivative (0.1 mole) was added gradually, the rate of addition being regulated so that the ether was maintained at a vigorous boil. A precipitate of sodium derivative and sodium chloride formed gradually. The addition of the dichloro compound required 30-90 minutes, and when this was complete the reaction mixture was heated in a water bath to complete the reaction. It was then cooled with a freezing mixture and stirred while water was added cautiously. The ether layer was separated and dried. The monosubstituted acetylene formed was isolated by fractionation.

Action of Sodium on 1,1-Dichloro-9-ethylthio-1-nonene. When 22 g of 1,1-dichloro-9-ethylthio-1-nonene was treated with 7.5 g of sodium, 30 ml of hydrogen separated. When the reaction mixture was treated with water, 1100 ml of hydrogen was collected (theory requires 1050 ml). The ethereal solution was washed with water and dried with calcium chloride. Vacuum distillation yielded 14.2 g (90%) of 9-ethylthio-1-nonyne, b.p. 129-130° (12 mm); n_D^{20} 1.4771; d_4^{20} 0.8854.

4,5,5-Trichloro-N,N-diethyl-4-pentenylamine. A solution of 22 g of 1,1,2,5- tetrachloro-1-pentene and 20 g of diethylamine in 60 ml of methanol was heated in an autoclave at 100-110° for 5-6 hours. Excess of diethylamine and methanol was removed from a water bath, and the residue was treated with dilute hydrochloric acid. The undissolved oil was extracted with ether. The hydrochloric acid solution was rendered alkaline with cooling, and was then extracted with ether. Vacuum distillation yielded 19.8 g (76%) of 4,4,5-trichloro-N,N-diethyl-4-pentenylamine, b.p. 84-85° (2 mm); n_D^{20} 1.4886; d_4^{20} 1.1378; Found MR 61.98; Calculated MR 61.84.

Found %: N 5.90; 5.89

$C_9H_{16}Cl_3N$. Calculated %: N 5.73

Its oxalate melted at 125-126° (from alcohol-ether)

Found %: N 4.34; 4.34

$C_{11}H_{18}Cl_3NO_4$. Calculated %: N 4.18

N,N-Diethyl-4- pentynylamine. A small amount of an ethereal solution of 4,5,5-trichloro-N,N-diethyl-4-pentenylamine was added to a mixture of 5.3 g of finely granulated sodium and 50 ml of ether. When the mixture had been heated, with stirring, for 15 minutes, reaction set in and the ether boiled without external application of heat. The remainder of the trichloro compound was then added dropwise. At first the reaction mixture acquired a dirty dark-blue color, but toward the end of the reaction it became white. The mixture was heated until the sodium disappeared, and it was then cooled and decomposed with water. The product was 7 g (88%) of N,N-diethyl-4-pentynylamine, b.p. 54° (10 mm); n_D^{20} 1.4412.

Action of Sodium on (3,3-Dichloroallyl)benzene. Treatment of 32 g of (3,3-dichloroallyl)benzene with 13 g of sodium by the usual method yielded 8 g of a product boiling at 60-65° (11 mm) and a large amount of nondistilling residue. Fractionation yielded a compound having b.p. 69-70° (11 mm), n_D^{20} 1.5800; d_4^{20} 0.9360; it appeared to be phenylpropadiene.

Found %: C 93.42; 93.23; H 6.93; 7.02

C_9H_8. Calculated %: C 93.10; H 6.90

When hydrogenated, it absorbed two molecular proportions of hydrogen.

2-Hexynoic Acid. Solid carbon dioxide was added to the reaction mixture obtained by the action of 12 g of sodium on 20 g of 1,1-dichloro-1-pentene. After the mixture had been decomposed with water, the aqueous layer was acidified with hydrochloric acid, and the oil that separated was extracted with ether. Vacuum distillation yielded 5.2 g (32%) of 2-hexynoic acid, b.p. 116-117° (13 mm) and n_D^{20} 1.4642. The literature [10] gives b.p. 120° (16 mm), n_D^{20} 1.4650, and m.p. 27°.

6-Diethylamino-1-phenyl-2-hexyn-1-ol. A solution of 8 g of benzaldehyde in 10 ml of ether was added, with cooling and stirring, to the reaction mixture obtained by treating 11 g of 5,5-dichloro-N,N-diethyl-4-pentenylamine with 8.6g of sodium. The mixture was heated in a water bath for 30 minutes, cooled, and decomposed with water. The ethereal solution was extracted with dilute hydrochloride acid . The hydrochloric acid solution was rendered alkaline, and the oil that separated was extracted with ether. Distillation yielded 5.2 g of 6-diethylamino-1-phenyl-2-hexyn-1-ol, b.p. 172-173° (2 mm); n_D^{20} 1.5327; d_4^{20} 1.0006; Found MR 75.96; Calculated MR 75.97.

Found %: N 5.89; 5.99

$C_{16}H_{23}NO$. Calculated %: N 5.72

6-Ethoxy-1-phenyl-2-hexyn-1-ol. 5-Ethoxy-1-pentyne (9.5 g) was added gradually to an ethereal solution of ethylmagnesium bromide (prepared from 12.5 g of ethyl bromide and 2.8 g of magnesium). The solution was heated until ethane ceased to be evolved. Benzaldehyde (15 g) was then added gradually with cooling and stirring, after which the mixture was heated for one hour, cooled, and decomposed with saturated ammonium chloride solution. Vacuum distillation yielded 16.1 g (87%) of 6-ethoxy-1-phenyl-2-hexyn-1-ol, b.p. 185-186° (3 mm); n_D^{20} 1.5265; d_4^{20} 1.0284.

Found %: C 77.24; 77.22; H 8.20; 8.23

$C_{14}H_{18}O_2$. Calculated %: C 77.08; H 8.25

SUMMARY

1. The action of sodium on 2,2-dichlorovinyl derivatives was studied, and it was shown that monosubstituted acetylenes were formed in 60-80% yield in most of the cases investigated.

2. A mechanism is proposed for the conversion of a $CCl_2 = CH$ group into an $HC \equiv C$ group by the action of sodium.

LITERATURE CITED

[1] A. Pinner, Ann. 179, 49 (1875); Ber. 8, 898 (1875).

[2] A. Pinner, Ber. 8, 1282 (1875).

[3] A. Pinner, Ber. 14, 1081 (1881).

[4] A. N. Nesmeyanov and L. I. Zakharkin, Bull. Acad. Sci., USSR, Div. Chem. Sci., 1953,988. (T.p. 879)* .

[5] Brit. Pat. 581901, C.A. 1947, 2428; U.S. Pat. 2,410,541, C.A. (1947), 981.

[6] A. Kirrmann, Comptes rend., 181,671 (1925).

[7] E. A. Braude, J. Coles, J. Chem. Soc., 1950, 179.

[8] R. Truchet, Ann. d. Chim. 16, 349 (1931).

[9] A. N. Nesmeyanov, R. Kh. Freidlina, and L. I. Zakharkin, Proc. Acad. Sci., USSR, 97, 91 (1954).

[10] A. E. Favorsky, J. prakt. Chem. (2), 37, 420 (1888); M. Bourguel Ann. d. Chim. (10) 3, 386 (1925.

Received January 21,1955

Institute of Heteroorganic Compounds
of the USSR Academy of Sciences

---

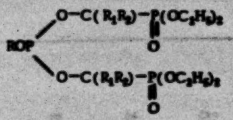
* T.p. = C. B. Translation pagination

SYNTHESIS OF ALKYL BIS[1-(DIETHOXYPHOSPHINYL)ALKYL] PHOSPHITES

P. I. Alimov and I. V. Cheplanova

Triesters of phosphorous acid were first prepared in the middle of the last century, and since then many compounds of this class have been synthesized [1]. Study of mixed phosphorous triesters began comparatively recently (1930-1940); mixed esters reported include alkyl diaryl and dialkyl aryl phosphites [2], 2-chloroethyl diethyl and bis(2-chloroethyl) ethyl phosphites [3], and also cyclic esters alkyl alkylene phosphites (glycol derivatives) and alkyl (aryl) arylene phosphites (pyrocatechol derivatives) [4]. *

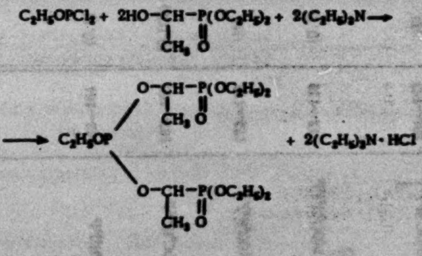
This paper describes the syntheses of organophosphorus compounds containing three phosphorus atoms, their general formula being



(R and R_1 are alkyl groups, and R_2 is H or alkyl).

These compounds can be regarded as mixed phosphorous esters – alkyl bis[1-(diethoxyphosphinyl)alkyl] phosphites – in which one ester grouping contains an aliphatic alcohol residue and the other two contain residues of a diethyl 1-hydroxyalkylphosphonate.

The substances were synthesized by reaction of alkyl phosphorodichloridites with diethyl 1-hydroxyalkylphosphonates in presence of tertiary amines for the binding of hydrogen chloride, for example:



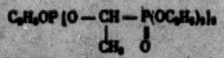
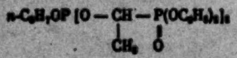
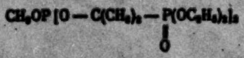
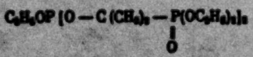
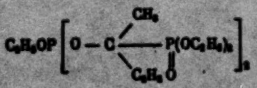
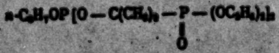
The reaction was carried out in an organic solvent – ether or gasoline – at first at room temperature, and then at 50-60°. The reactants used were the diethyl esters of 1-hydroxyethyl-, 1-hydroxy-1-methylethyl-, and 1-hydroxy-1-methylpropyl-phosphonic acids, which were prepared by Abramov's method [5], and the methyl, ethyl, and propyl esters of phosphorodichloridous acid. The table gives the formulas, physical constants, and yields of the products.

The substances listed in the table are colorless mobile liquids having a feeble ethereal odor; they are soluble in water and in organic solvents. The experimentally determined molecular refractions of these compounds are lower – by one unit, on the average – than the calculated values. These discrepancies are probably to be attributed to changes in the atomic refraction of phosphorus arising from peculiarities in the structures of the compounds. In the molecular refraction calculations we took the atomic refraction of phosphorus to be 7.04 for the tervalent state and 4.27 for phosphorus in the alkylphosphonic residue [6].

---

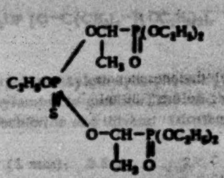
* This statement is obsure, but is clarified by reference to abstracts of original papers – Publishers

TABLE

No.	Formula	B.p. (°C)	Pressure (mm)	n_D^{20}	d_4^{20}	MR		Yield (%)
						Found	Calculated	
1	 $C_2H_5OP[O-\underset{CH_3}{\underset{\mid}{CH}}-\underset{O}{\underset{\|}{P}}(OC_2H_5)_2]_2$	162—164	(0.1)	1.4479	1.1579	101.3	101.7	28.9
2	 $n\text{-}C_3H_7OP[O-\underset{CH_3}{\underset{\mid}{CH}}-\underset{O}{\underset{\|}{P}}(OC_2H_5)_2]_2$	167—168	(0.035)	1.4477	1.1476	105.3	106.3	33.6
3	 $CH_3OP[O-C(CH_3)_2-\underset{O}{\underset{\|}{P}}(OC_2H_5)_2]_2$	172—173	(1)	1.4505	1.1592	104.9	106.32	28.7
4	 $C_2H_5OP[O-C(CH_3)_2-\underset{O}{\underset{\|}{P}}(OC_2H_5)_2]_2$	172—173	(0.5)	1.4500	1.1370	110.1	110.9	34
5		181—183	(1)	1.4562	1.1303	118.8	120.18	9.9
6	 $n\text{-}C_3H_7OP[O-C(CH_3)_2-\underset{O}{\underset{\|}{P}}-(OC_2H_5)_2]_2$	175—176	(0.35)	1.4494	1.1243	114.6	115.6	80.1

Alkyl bis[1-(diethoxyphosphinyl)alkyl] phosphites are hydrolyzed by dilute hydrochloric acid at the boil with formation of phosphorous acid and 1-hydroxyalkylphosphonic acids. Phosphorous acid, so formed, was determined quantitatively by a method based on its ability to reduce mercuric chloride to mercurous chloride [7].

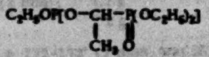
Being tervalent phosphorus derivatives, alkyl bis[1-(diethylphosphinyl)alkyl] phosphites readily unite with cuprous halides [8] and with sulfur [9]. The latter reaction yields O-alkyl O,O-bis[1-(diethoxyphosphinyl)alkyl] phosphorothioates, for example:



EXPERIMENTAL

I. Synthesis of Alkyl Bis[1-(diethoxyphosphinyl) alkyl] Phosphites

1. Ethyl Bis[1-(diethoxyphosphinyl)ethyl] Phosphite



$$C_2H_5OP[O-\underset{CH_3}{\underset{|}{CH}}-\underset{O}{\underset{\|}{P}}(OC_2H_5)_2]_2$$

A mixture of 28 g of diethyl 1-hydroxyethylphosphonate [5] (b.p. 130-131°/6 mm), 14.4 g of triethylamine, and 140 ml of gasoline (b.p. 75-125°) was prepared in a three-necked, round-bottomed flask fitted with mechanical stirrer, dropping funnel, and reflux condenser. Ethyl phosphorodichloridite (10.5 g) was added gradually from the dropping funnel at room temperature. Triethylamine hydrochloride then separated. When addition of the dichloridite was complete, the reaction mixture was stirred for two hours at a bath temperature of 50-60°. When the mixture was cool, triethylamine hydrochloride was filtered off and washed with ether. After removal of solvent a residue (30.2 g, i.e. 96.4%) of light-yellow mobile liquid remained. Distillation from an Arbuzov flask gave the following fractions:

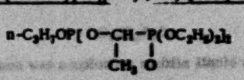
Fraction I	b.p. 115-160° (0.1 - 0.075 mm);	6.5 g
Fraction II	b.p. 160-165° (0.075 mm);	13.9 g
Residue		7.3g

Redistillation of Fraction II yielded 12.2 g of a substance having the following constants: b.p. 162-164° (0.1 mm); n_D^{20} 1.4479, d_4^{20} 1.1579; The yield was 38.9%.
Found MR 101.3, Calculated $C_{14}H_{33}P_3O_9$ MR 101.7.

	Found %:	P 21.18; 21.35
$C_{14}H_{33}P_3O_9$.	Calculated %:	P 21.23

This substance was a colorless, almost odorless, highly mobile liquid, readily soluble in water, ether, alcohol, and other organic solvents.

2. Propyl Bis[1-(diethoxyphosphinyl)ethyl] Phosphite



$$n\text{-}C_3H_7OP[O-\underset{CH_3}{\underset{|}{CH}}-\underset{O}{\underset{|}{P}}(OC_2H_5)_2]_2$$

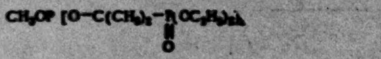
The reactants were diethyl 1-hydroxyethylphosphonate (21 g), triethylamine (11.7 g), and propyl phosphorodichloridite (9.3 g). The reaction conditions were as in the first experiment. After removal of triethylamine hydrochloride and solvent, there was a residue, amounting to 25.8 g (99.2%), of a light-yellow mobile liquid. Distillation yielded the fractions.

Fraction I	b.p. 110-167° (0.05-0.035 mm);	10.5 g
Fraction II	b.p. 167-168° (0.035 mm);	8.8 g
Fraction III	b.p. 168-174° (0.035 mm);	2.9 g
Residue		2.1 g

The yield of Fraction II was 33.3%; it had n_D^{20} 1.4477; d_4^{20} 1.1476; Found MR 105.3; Calculated $C_{15}H_{35}P_3O_9$ MR 106.3.

	Found %: P 20.90; 20.92
$C_{15}H_{35}P_3O_9$.	Calculated %: P 20.57

3. Methyl Bis[1-(diethoxyphosphinyl)-1-methylethyl] Phosphite


$$CH_3OP[O-C(CH_3)_2-\underset{\underset{O}{\|}}{P}(OC_2H_5)_2]_2$$

Reaction of 25 g of diethyl 1-hydroxy-1-methylethylphosphonate [5] (b.p. 130-131°, 10 mm), 8.5 g of methyl phosphorodichloridite, and 13 g of triethylamine in gasoline (130 ml; b.p. 75-125°) solution yielded 29 g of crude product after removal of triethylamine hydrochloride and solvent. Distillation yielded the fractions:

Fraction I	b.p.	105 - 155° (1 mm);	3.8 g
Fraction II	b.p.	155 - 176° (1 mm);	19.8 g
Residue			4 g

Redistillation of Fraction II gave:

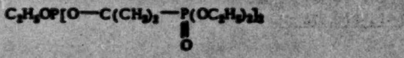
Fraction I	b.p.	60 - 172° (1 mm);	8.9 g
Fraction II	b.p.	172 - 173° (1 mm);	7.7 g
Residue			2 g

The yield of Fraction II, b.p. 172-173° (1 mm), was 26.7%. It had n_D^{20} 1.4505; d_4^{20} 1.1592; Found MR 104.9; Calculated $C_{15}H_{35}P_3O_9$ MR 106.32.

	Found %: P 20.93; 20.86
$C_{15}H_{35}P_3O_9$.	Calculated %: P 20.57

The substance was a colorless, highly mobile liquid having a feeble odor. It was readily soluble in water and in organic solvents.

4. Ethyl Bis[1-(diethoxyphosphinyl)-1-methylethyl] Phosphite


$$C_2H_5OP[O-C(CH_3)_2-\underset{\underset{O}{\|}}{P}(OC_2H_5)_2]_2$$

Reaction was between 25 g of diethyl 1-hydroxy-1-methylethylphosphonate, 12.9 g of triethylamine, and 9.4 g of ethyl phosphorodichloridite. The weight of crude product was 27.1 g (91.2%). Distillation yielded the fractions:

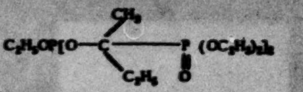
Fraction I	b.p.	105 - 158° (0.5 mm);	5.5 g
Fraction II	b.p.	158 - 176° (0.5 mm);	16.6 g
Residue			3 g

Distillation of Fraction II yielded 10.1 g (34%) of a substance having b.p. 172-173° (0.5 mm); n_D^{20} 1.4500; d_4^{20} 1.1379 Found MR 110.1; Calculated $C_{16}H_{37}P_3O_9$ MR 110.9

	Found %: P 20.19; 20.27
$C_{16}H_{37}P_3O_9$.	Calculated %: P 19.96

This substance was a colorless mobile liquid of feeble odor.

5. Ethyl Bis[1-(diethoxyphosphinyl)-1-methylpropyl] Phosphite


$$C_2H_5OP[O-\overset{CH_3}{\underset{C_2H_5}{C}}-\underset{\underset{O}{\|}}{P}(OC_2H_5)_2]_2$$

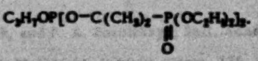
Reaction was between 25.8 g of diethyl 1-hydroxy-1-methylpropylphosphonate (b.p. 135-136°, 11 mm), 12.4 g of triethylamine, and 9 g of ethyl phosphorodichloridite. The yield of crude product was 28.8 g (95%). Distillation gave:

Fraction I b.p. 100 - 170° (0.1 - 0.04 mm); 14.9 g
Fraction II b.p. 170 - 174° (0.04 mm); 10 g

Redistillation of Fraction II gave 3 g (9.9%) of a substance having b.p. 181-183° (1 mm); n_D^{20} 1.4562; d_4^{20} 1.1303; Found MR 113.8; Calculated $C_{16}H_{41}P_3O_9$ MR 120.18.

	Found %: P 19.08; 19.14
$C_{18}H_{41}P_3O_9$.	Calculated %: P 18.82

6. Propyl Bis[1-(diethoxyphosphinyl)-1-methylethyl] Phosphite



$$C_3H_7OP[O-C(CH_3)_2-\underset{\underset{O}{\|}}{P}(OC_2H_5)_2]_2.$$

After reaction between 24.3 g of diethyl 1-hydroxy-1-methylethylphosphonate, 12.5 g of triethylamine, and 10 g of propyl phosphorodichloridite and removal of triethylamine hydrochloride and solvent, 28.3 g (95.2%) of crude product was obtained. Distillation yielded the fractions:

Fraction I b.p. 90 - 175° (0.35 mm); 10.2 g
Fraction II b.p. 175 - 176° (0.35 mm); 14.9 g

The yield of Fraction II was 50.1%, and it had n_D^{20} 1.4494; d_4^{20} 1.1243; Found MR 114.6; Calculated $C_{17}H_{39}P_3O_9$ MR 115.6.

	Found %: P 19.65; 19.67
$C_{17}H_{39}P_3O_9$.	Calculated %: P 19.38

It was a colorless mobile liquid, sparingly soluble in water, but readily soluble in organic solvents.

II. Reactions of Alkyl Bis[1-(diethoxyphosphinyl)alkyl] Phosphites

1. Hydrolysis of Propyl Bis[1-(diethoxyphosphinyl)-1-methylethyl] Phosphite. A solution of 0.5833 g of the mixed ester (b.p. 175-176°, 0.35 mm) in 15 ml of 10% hydrochloric acid was boiled for 6 hours 30 minutes. An aqueous solution of 1.5 g (125% excess) of mercuric chloride was added to the hydrolysis products, and the mixture was then stirred at the boiling point for some time. Calomel, amounting to 0.5696 g (99.28%), was obtained.

2. Addition of Cuprous Iodide to Ethyl Bis[1-(diethoxyphosphinyl)-1-methylethyl] Phosphite. Cuprous iodide (0.408 g) was added to 1 g (an equimolecular proportion) of the mixed ester (b.p. 172-173°, 0.5 mm). The mixture was heated to 145-150°, and almost the whole of the salt went into solution. The product was a thick clear liquid which did not crystallize after prolonged standing.

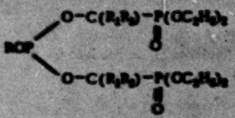
3. Addition of Sulfur to Ethyl Bis[1-(diethoxyphosphinyl)ethyl] Phosphite. Sulfur powder (0.1333 g) was added to 1.8247 g of the mixed ester (b.p. 162-164°, 0.1 mm; n_D^{20} 1.4595; d_4^{20} 1.1937; Found MR 107.7; Calculated $C_{14}H_{33}P_3O_9S$ MR 108.075.

	Found %: P 19.95; 19.82
$C_{14}H_{33}P_3O_9S$.	Calculated %: P 19.70

The product was a thick, colorless, almost odorless liquid. It was soluble in organic solvents, but only sparingly soluble in water.

SUMMARY

1. The synthesis is described of mixed phosphorous esters in which diethoxyphosphinyl groups are present as substituents in the hydrocarbon radicals, i.e. alkyl bis[1-(diethoxyphosphinyl)alkyl] phosphites:



(R is CH_3, C_2H_5 or n-C_3H_7; R_1 is H or CH_3; and R_2 is CH_3 or C_2H_5).

2. Some of the properties of these mixed esters are described.

LITERATURE CITED

[1] V. M. Plets, Organic Compounds of Phosphorus, Defense Press, 1940, 272; G. M. Kosolapoff, Organophosphorous Compounds, 1950, p. 180.

[2] M. I. Kabachnik, Bull. Acad. Sci., USSR, Div. Chem. Sci., 1947, 631, T. Milobendzki, K. Szulgin, Chem. Polsk. 15, 66 (1917).

[3] M. I. Kabachnik, and P. A. Rossiiskaya, Bull. Acad. Sci., USSR, Div. Chem. Sci., 1948, No. 1, 95.

[4] L. Anschütz, H. Walbrecht, J. prakt. Chem. 133, 65 (1932); A. E. Arbuzov and F. G. Valitova, Bull. Acad. Sci., USSR, Div. Chem. Sci., 1940, 529; A. E. Arbuzov, V. M. Zoroastrova and N. I. Rizpolozhensky, Bull. Acad. Sci., USSR, Div. Chem. Sci., 1948, No. 2, 208; P. A. Rossiiskaya and M. I. Kabachnik, Bull. Acad. Sci., USSR, Div. Chem Sci., 1947, No. 5, 509.

[5] V. S. Abramov, J. Gen. Chem. 22, No. 4, 647 (1952) (T.p. 709)* .

[6] M. I. Kabachnik, Bull. Acad. Sci., USSR, Div. Chem. Sci., 1948, No. 2, 220.

[7] F. P. Treadwell and W. T. Hall, Qualitative Analysis, State Chem. Press, 1946, p. 428.

[8] A. E. Arbuzov, Selected Works, Acad. Sci., USSR Press, 1952, p. 88.

[9] P. S. Pishchimuka, J. Russ. Chem. Soc. 44, 1429 (1912).

Received December 7, 1954

A. E. Arbuzov Chemical Institute of the
Kazan Affiliated Institute of the USSR
Academy of Sciences

---

* T.p. = C.B. Translation pagination

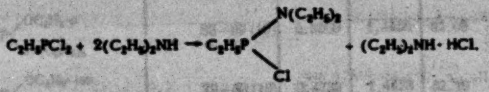
ESTERS OF ETHYLPHOSPHONOUS ACID, AND SOME OF THEIR REACTIONS

COMMUNICATION 6. TRIETHYLPHOSPHONAMIDOUS ESTERS

B. A. Arbuzov, N. I. Rizpolozhensky, and M. A. Zvereva

In continuation of our work on the properties of ethylphosphonous esters, we have synthesized triethylphosphonamidous esters and studied some of their properties. The results of this work are described in the present paper. These esters have not been described previously in the literature.

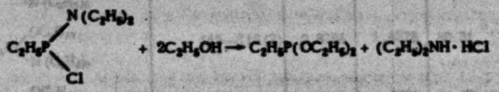
The triethylphosphonamidous esters were synthesized from triethylphosphonamidous chloride, which was itself prepared by the action of diethylamine on ethylphosphonous dichloride in a medium of absolute ether:



$$C_2H_5PCl_2 + 2(C_2H_5)_2NH \rightarrow C_2H_5P\begin{matrix}N(C_2H_5)_2\\ Cl\end{matrix} + (C_2H_5)_2NH\cdot HCl.$$

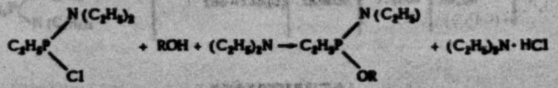
The yield of the acid chloride was about 80%. Triethylphosphonamidous chloride is colorless mobile liquid which fumes strongly in the air. It is very rapidly decomposed by atmospheric moisture with the separation of diethylamine hydrochloride. The acid chloride has a very unpleasant, penetrating odor.

When triethylphosphonamidous chloride is treated with ethanol in a medium of absolute ether, diethyl ethylphosphonite and diethylamine hydrochloride are formed. This reaction can be expressed by the equation:



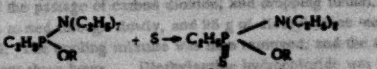
$$C_2H_5P\begin{matrix}N(C_2H_5)_2\\ Cl\end{matrix} + 2C_2H_5OH \rightarrow C_2H_5P(OC_2H_5)_2 + (C_2H_5)_2NH\cdot HCl$$

Triethylphosphonamidous esters were prepared by the action of alcohols on triethylphosphonamidous chloride in a medium of absolute ether in presence of triethylamine:



$$C_2H_5P\begin{matrix}N(C_2H_5)_2\\ Cl\end{matrix} + ROH + (C_2H_5)_2N \rightarrow C_2H_5P\begin{matrix}N(C_2H_5)\\ OR\end{matrix} + (C_2H_5)_3N\cdot HCl$$

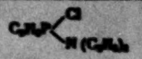
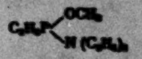
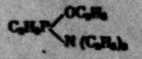
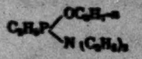
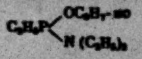
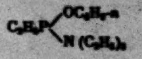
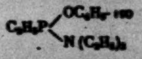
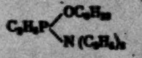
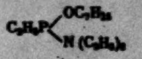
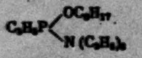
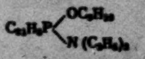
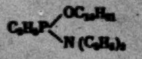
In this way triethylphosphonamidous esters, ranging from the methyl to the decyl ester, were prepared in yields ranging from 77% down to 22% (Table 1). Triethylphosphonamidous esters are colorless mobile liquids having an unpleasant phosphine odor. They readily combine with sulfur with formation of O-esters of triethylphosphonamidothioic acid:



$$C_2H_5P\begin{matrix}N(C_2H_5)_2\\ OR\end{matrix} + S \rightarrow C_2H_5\underset{\underset{S}{\parallel}}{P}\begin{matrix}N(C_2H_5)_2\\ OR\end{matrix}$$

In this way previously undescribed O-esters of triethylphosphonamidothioic acid — ranging from the methyl to the decyl ester — were prepared. The principal constants of these esters are given in Table 2. O-Alkyl triethylphosphonamidothioates are colorless mobile liquids of unpleasant odor. They are insoluble in water, but readily soluble in alcohol, ether, gasoline, and benzene.

TABLE 1

No.	Formula	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	Found MR	Calculated MR	Yield (%)
1	 $C_2H_5P(Cl)N(C_2H_5)_2$	52—53 (2)	~0.9904	~1.4828	—	—	77
2	 $C_2H_5P(OCH_3)N(C_2H_5)_2$	40—50 (10)	0.8954	1.4450	48.44	48.20	72
3	 $C_2H_5P(OC_2H_5)N(C_2H_5)_2$	53—54 (9)	0.8847	1.4418	53.80	52.82	68
4	 $C_2H_5P(OC_3H_7\text{-}n)N(C_2H_5)_2$	73—74 (10)	0.8820	1.4439	57.70	57.44	65
5	 $C_2H_5P(OC_3H_7\text{-}iso)N(C_2H_5)_2$	63—65 (10)	0.8730	1.4400	57,89	57.44	61
6	 $C_2H_5P(OC_4H_9\text{-}n)N(C_2H_5)_2$	88—89 (10)	0.8800	1.4450	62.09	62.15	61.7
7	 $C_2H_5P(OC_4H_9\text{-}iso)N(C_2H_5)_2$	79—80 (10)	0.8739	1.4423	62.19	62.15	71
8	 $C_2H_5P(OC_6H_{13})N(C_2H_5)_2$	80—81 (1)	0.8787	1.4500	71.37	71.29	61
9	 $C_2H_5P(OC_7H_{15})N(C_2H_5)_2$	101—102 (1)	0.8794	1.4513	75.72	75.21	40
10	 $C_2H_5P(OC_8H_{17})N(C_2H_5)_2$	115—118 (2)	0.8794	1.4528	80.31	80.53	30
11	 $C_{21}H_5P(OC_9H_{19})N(C_2H_5)_2$	121—122 (2)	0.8800	1.4550	84.93	85.15	27
12	 $C_2H_5P(OC_{10}H_{21})N(C_2H_5)_2$	134—135 (2)	0.8808	1.4569	89.80	89.76	22

EXPERIMENTAL

I. Synthesis of Triethylphosphonamidous Esters

1. **Triethylphosphonamidous Chloride.** A mixture of 85 g of ethylphosphonous dichloride and 500 ml of absolute ether was prepared in a 750-ml four-necked flask fitted with mercury-sealed mechanical stirrer, reflux condenser, tube for the passage of carbon dioxide, and dropping funnel. The flask was cooled with ice and salt, carbon dioxide was passed through slowly, and 95 g of diethylamine was added over a period of two hours from the dropping funnel. The cooling mixture was then removed, and the reaction products were stirred at room temperature for about three hours. Diethylamine hydrochloride was filtered off at the pump and washed several times on the filter with absolute ether.

Ether was distilled from the filtrate, and the residue was vacuum-fractionated, when triethylphosphonamidous chloride, b.p. 52-53° (3 mm), was isolated. It was obtained as a colorless mobile liquid having an unpleasant penetrating odor. It reacted with water with bursts of flame. The acid chloride decomposed very rapidly in the air with the separation of crystalline products (diethylamine hydrochloride). The density and refractive index of the acid chloride were measured in an atmosphere of dry carbon dioxide, but in spite of this precaution, decomposition of the acid chloride was observed in the pycnometer and more particularly, in the refractometer (precipitation of crystals). Our values for these constants are therefore not altogether accurate: $d_4^{20} \approx 0.9964$; $n_D^{20} \approx 1.4836$.

Found %: P 18.2; 18.25

$C_6H_{15}PNCl$. Calculated %: P 18.55

The yield of triethylphosphonamidous chloride was 83 g (77%).

2. Methyl Triethylphosphonamidite. The ester was synthesized in the apparatus described in detail above. A mixture of 2 g of methanol, 15 g of triethylamine, and 150 ml of absolute ether was prepared in the reaction flask. Triethylphosphonamidous chloride (21.5 g) was added from the dropping funnel over a period of one hour, the reaction flask being cooled with a freezing mixture. The cooling mixture was then removed, and the reaction products were stirred at room temperature for 2.5-3 hours. The precipitate of triethylamine hydrochloride was filtered off at the pump and washed three or four times with absolute ether.

Ether was distilled from the filtrate, and the residue was vacuum-fractionated from an Arbuzov flask. The methyl triethylphosphonamidite then obtained had b.p. 49-50° (10 mm); d_4^{20} 0.8954; n_D^{20} 1.4450.

Found MR 48.44

$C_7H_{18}PON$. Calculated MR 48.20

Found %: P 19.2; 19.25

$C_7H_{18}PON$. Calculated %: P 19.00

The yield of ester was 15.2 g (72%). Methyl triethylphosphonamidite is a colorless mobile liquid having a very unpleasant odor.

3. Ethyl Triethylphosphonamidite. In the preparation of this ester, and of all the remaining esters, the apparatus and procedure were essentially the same as for methyl triethylphosphonamidite. The reactants taken for the synthesis of the ethyl ester were 5.6 g of ethanol, 13.5 g (1.5 g excess) of triethylamine, and 20 g of triethylphosphonamidous chloride in 150 ml of absolute ether. Ethyl triethylphosphonamidite has b.p. 53-54° (9 mm); d_4^{20} 0.8847, n_D^{20} 1.4418.

Found MR 53.80

$C_8H_{20}PON$. Calculated MR 52.82

Found %: P 17.65; 17.68

$C_8H_{20}PON$. Calculated %: P 17.5

The ester has a very unpleasant odor. The yield was 13.3 g (63%).

4. Propyl Triethylphosphonamidite. The ester was prepared from 8.55 g of propyl alcohol, 16 g (1.6 g excess) of triethylamine, and 23.8 g of triethylphosphonamidous chloride in 150 ml of absolute ether. Vacuum fractionation yielded propyl triethylphosphonamidite having b.p. 73-74° (10 mm); d_4^{20} 0.8820; n_D^{20} 1.4439.

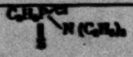
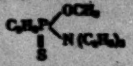
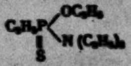
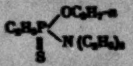
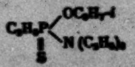
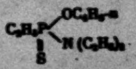
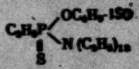
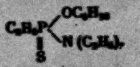
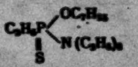
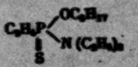
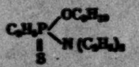
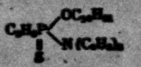
Found MR 57.70

$C_9H_{22}PON$. Calculated MR 57.44

The ester has an unpleasant odor. The yield was 17.2 g (65%).

5. Isopropyl Triethylphosphonamidite. The ester was prepared in 120 ml of absolute ether from 5.9 g of isopropyl alcohol, 11 g of triethylamine, and 16.1 g of triethylphosphonamidous chloride; its constants were b.p. 63-65° (9 mm); d_4^{20} 0.8730; n_D^{20} 1.4400.

TABLE 2

No.	Formula	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	Found MR	Calculated MR*	Yield (%)
1	 $C_2H_5P(S)(Cl)N(C_2H_5)_2$	94—95 (1)	1,1135	1,5305	54.55	54.85	80
2	 $C_2H_5P(S)(OCH_3)N(C_2H_5)_2$	112—113 (10)	1.0287	1.4882	54,63	54.84	80
3	 $C_2H_5P(S)(OC_2H_5)N(C_2H_5)_2$	115—116 (9)	1.0042	1.4828	59.48	59.55	73
4	 $C_2H_5P(S)(OC_3H_7\text{-}n)N(C_2H_5)_2$	84—85 (1)	0.9892	1.4801	64.13	64.17	65
5	 $C_2H_5P(S)(OC_3H_7\text{-}i)N(C_2H_5)_2$	118.5—119 (9)	0.9858	1.4781	64.13	64.17	67,5
6	 $C_2H_5P(S)(OC_4H_9\text{-}n)N(C_2H_5)_2$	88—89 (1)	0.9789	1.4785	68.67	68.79	61.1
7	 $C_2H_5P(S)(OC_4H_9\text{-iso})N(C_2H_5)_2$	132—133 (13)	0,9739	1.4750	68.60	68.79	63
8	 $C_2H_5P(S)(OC_6H_{13})N(C_2H_5)_2$	132—133 (1.5)	0.9642	1.4790	78.64	78.73	49.5
9	 $C_2H_5P(S)(OC_7H_{15})N(C_2H_5)_2$	137—137.5 (2)	0.9578	1.4789	82.74	82.65	32
10	 $C_2H_5P(S)(OC_8H_{17})N(C_2H_5)_2$	144—144.5 (1)	0.9516	1.4793	87.45	87.27	33.4
11	 $C_2H_5P(S)(OC_9H_{19})N(C_2H_5)_2$	151—152 (1)	0.9495	1.4796	91.91	91.88	25.6
12	 $C_2H_5P(S)(OC_{10}H_{21})N(C_2H_5)_2$	170—172 (2.5)	0.9446	1.4800	96.67	96.51	19.2

---

* The atomic refraction of nitrogen was taken to be 2.09₁; the atomic refraction of phosphorus calculated from the results of the present work is 4.78 [1].

Found MR 57.50

$C_9H_{22}OPN$. Calculated MR 57.44

Found %: P 16.35; 16.21

$C_9H_{22}OPN$. Calculated %: P 16.1

The yield of ester was 11.3 g (61%).

6. Butyl Triethylphosphonamidite. The substances taken for reaction were 6 g of butyl alcohol, 9.5 g of triethylamine, 120 ml of absolute ether, and 15.5 g of triethylphosphonamidous chloride. The constants of butyl triethylphosphonamidite are b.p. 88-89° (10 mm); d_4^{20} 0.8800; n_D^{20} 1.4450.

Found MR 62.09

$C_{10}H_{24}OPN$. Calculated MR 62.15

Found %: P 15.26; 15.15

$C_{10}H_{24}OPN$. Calculated %: P 15.1

The yield of ester was 11.7 g (61.7%).

7. Isobutyl Triethylphosphonamidite. This was prepared from 7.3 g of isobutyl alcohol, 12 g of triethylamine (2 g excess), and 16.6 g of triethylphosphonamidous chloride in 130 ml of absolute ether. The constants of the ester are b.p. 79-80° (10 mm); d_4^{19} 0.8739; n_D^{20} 1.4423.

Found MR 62.19

$C_{10}H_{24}OPN$. Calculated MR 62.15

Found %; P 15.15; 15.17

$C_{10}H_{24}OPN$. Calculated %: P 15.1

The yield of ester was 13.5 g (71%).

8. Hexyl Triethylphosphonamidite. This was prepared from 8 g of hexyl alcohol, 9 g of triethylamine, and 13.1 g of triethylphosphonamidous chloride in 100 ml of absolute ether. The hexyl triethylphosphamidite so obtained had b.p. 80-81° (1 mm); d_4^{20} 0.8787; n_D^{20} 1.4500.

Found MR 71.37

$C_{12}H_{28}PON$. Calculated MR 71.29

Found %; P 13.61; 13.50

$C_{12}H_{28}PON$. Calculated %: P 13.32

The yield of ester was 11.1 g (61%).

9. Heptyl Triethylphosphonamidite. This ester was prepared from 9 g of heptyl alcohol, 8.5 g of triethylamine, and 12.8 g of triethylphosphonamidous chloride in 100 ml of absolute ether. The heptyl triethylphosphonamidite so obtained had b.p. 101-102° (1 mm); d_4^{20} 0.8794; n_D^{20} 1.4513.

Found MR 75.73

$C_{13}H_{30}PON$. Calculated MR 75.21

Found %: P 12.31; 12.38

$C_{13}H_{30}PON$. Calculated %: P 12.58

The yield of ester was 7.6 g (40%).

10. Octyl Triethylphosphonamidite. This ester was prepared from 10.3 g of octyl alcohol, 9.5 g of triethylamine, and 13.2 g of triethylphosphonamidous chloride in 100 ml of absolute ether. The ester obtained had b.p. 115-116° (2 mm); d_4^{20} 0.8794; n_D^{20} 1.4528.

Found MR 80.31

$C_{14}H_{32}PON$. Calculated MR 80.53

Found %: P 12.22; 12.18

$C_{14}H_{32}PON$. Calculated %: P 11.9

The yield of ester was 3.2 g (30%).

11. Nonyl Triethylphosphonamidite. The nonyl ester was prepared from 10.8 g of nonyl alcohol, 8.5 g of triethylamine, and 16 g of triethylphosphonamidous chloride in 100 ml of absolute ether. The ester obtained had the following constants: b.p. 121-122° (2 mm); d_4^{20} 0.8800; n_D^{20} 1.4550.

Found MR 84.93
$C_{15}H_{34}PON$. Calculated MR 85.15
Found %: P 11.60; 11.51
$C_{15}H_{34}PON$. Calculated %: P 11.30

The yield of ester was 7.1 g (27%).

12. Decyl Triethylphosphonamidite. The decyl ester was prepared from 12.5 g of decyl alcohol, 9 g of triethylamine, and 13.2 g of triethylphosphonamidous chloride in 100 ml of absolute ether. The decyl triethylphosphonamidite so obtained had the following constants: b.p. 134-135° (2 mm); d_4^{20} 0.9806; n_D^{20} 1.4509.

Found MR 89.50
$C_{16}H_{36}PON$. Calculated MR 89.76

The yield of ester was 5.4 g (22%).

II. Synthesis of O-Alkyl Triethylphosphonamidothioates

1. Triethylphosphonamidothioic Chloride. Triethylphosphonamidous chloride (9.2 g) was placed in a three-necked flask fitted with reflux condenser, thermometer, and tube for the passage of carbon dioxide. Sulfur powder (1.75 g) was added in portions to the acid chloride. The reaction did not go in the cold, and when the mixture was heated to 120° some of the sulfur dissolved, but it was reprecipitated on cooling. A few crystals of aluminum chloride were then added, and reaction began immediately. The temperature in the flask begain to rise rapidly, attaining 170° toward the end of the reaction, and the contents became brown. Vacuum distillation of the reaction products from an Arbuzov flask yielded triethylphosphonamidothioic chloride, b.p. 94-95° (1 mm); n_D^{20} 1.1135; d_4^{20} 1.5205.

Found MR 54.55
$C_6H_{15}PNSCl$. Calculated MR 54.68
Found %: P 15.82; 15.6
$C_6H_{15}PNCl$. Calculated %: P 15.55

The yield of acid chloride was 8.8 g (80%).

2. O-Methyl Triethylphosphonamidothioate. Methyl triethylphosphonamidite (4.5 g) was placed in a three-necked flask fitted with thermometer, tube for the passage of carbon dioxide, and reflux condenser. Addition of sulfur to the ester was found to proceed very vigorously, and the sulfur was therefore added in small portions. The final portions of sulfur reacted sluggishly, but at 140-150° the whole (0.89 g) of the sulfur taken for reaction dissolved. Vacuum distillation of the reaction product yielded O-methyl triethylphosphonamidothioate, b.p. 112-113° (10 mm); d_4^{20} 1.0287; n_D^{20} 1.4882.

Found MR 54.63
$C_7H_{18}PONS$. Calculated MR 54.84
Found %: P 15.82; 15.9; S 16.21; 16.15
$C_7H_{18}PONS$. Calculated %: P 15.79 S 16.06

The yield of ester was 3.7 g (69%).

3. O-Ethyl Triethylphosphonamidothioate. The above-described procedure was followed. The reactants were ethyl triethylphosphonamidite (4.1 g) and sulfur (0.75 g). Vacuum fractionation of the reaction products from an Arbuzov flask yielded O-ethyl triethylphosphonamidothioate, b.p. 115-116° (9 mm); d_4^{20} 1.0042; n_D^{20} 1.4828.

Found MR 59.48
$C_8H_{20}PONS$. Calculated MR 59.55
Found %: P 15.0; 14.95
$C_8H_{20}PONS$. Calculated %: P 14.82

The yield of ester was 3.6 g (75%).

4. O-Propyl Triethylphosphonamidothioate. The reactants were propyl triethylphosphonamidite (5 g) and sulfur (0.8 g). Vacuum distillation of the reaction product from an Arbuzov flask gave O-propyl triethylphosphonamidothioate, b.p. 84-85° (1 mm); d_4^{20} 0.9892; n_D^{20} 1.4801.

	Found MR 64.13
$C_9H_{22}PONS$.	Calculated MR 64.17
	Found %: P 14.11; 14.18
$C_9H_{22}PONS$.	Calculated %: P 13.9

The yield of ester was 3.8 g (65%).

5. O-Isopropyl Triethylphosphonamidothioate. The reactants were isopropyl triethylphosphonamidite (4.7 g) and flowers of sulfur (0.78 g). Vacuum fractionation of the reaction product from an Arbuzov flask gave O-isopropyl triethylphosphonamidothioate, b.p. 118.5-119° (9 mm); d_4^{20} 0.9858; n_D^{20} 1.4781.

	Found MR 64.13
$C_9H_{22}PONS$.	Calculated MR 64.17
	Found %: P 14.05; 14.12
$C_9H_{22}PONS$.	Calculated %: P 13.9

The yield of ester was 3.7 g (67.5%).

6. O-Butyl Triethylphosphonamidothioate. The ester was prepared from 6.2 g of butyl triethylphosphonamidite and 0.97 g of flowers of sulfur. Vacuum fractionation from an Arbuzov flask gave O-butyl triethylphosphonamidothioate, b.p. 88-89° (1 mm); d_4^{20} 0.9739; n_D^{20} 1.4750.

	Found MR 68.67
$C_{10}H_{24}PONS$.	Calculated MR 69.79
	Found %: P 13.28; 13.11
$C_{10}H_{24}PONS$.	Calculated %: P 13.18

The yield of ester was 4.4 g (61%).

7. O-Isobutyl Triethylphosphonamidothioate. The ester was prepared from 4 g of isobutyl triethylphosphonamidite and 0.62 g of flowers of sulfur. Vacuum distillation from an Arbuzov flask gave O-isobutyl triethylphosphonamidothioate, b.p. 132-133° (13 mm); d_4^{20} 0.9739; n_D^{20} 1.4750.

	Found MR 68.60
$C_{10}H_{24}PONS$.	Calculated MR 68.79
	Found %: P 13.31; 13.22
$C_{10}H_{24}PONS$.	Calculated %: P 13.18

The yield of ester was 2.9 g (63%).

8. O-Hexyl Triethylphosphonamidothioate. The ester was prepared from 6.4 g of hexyl triethylphosphonamidite and 0.88 g of sulfur. Vacuum distillation of the reaction product from an Arbuzov flask gave O-hexyl triethylphosphonamidothioate, b.p. 132-133° (1.5 mm); d_4^{20} 0.9642; n_D^{20} 1.4790.

	Found MR 78.64
$C_{12}H_{28}PONS$.	Calculated MR 78.73
	Found %: P 11.54; 11.72
$C_{12}H_{28}PONS$.	Calculated %: P 11.68

The yield of the ester was 3.6 g (49.5%).

9. O-Heptyl Triethylphosphonamidothioate. Reaction was between 3.2 g of heptyl triethylphosphonamidite and 0.41 g of flowers of sulfur. Vacuum distillation of the reaction product from an Arbuzov flask gave O-heptyl triethyl-

phosphonamidite, b.p. 137-137.5° (2 mm); d_4^{20} 0.9578; n_D^{20} 1.4789.

Found MR 82.74
$C_{13}H_{30}PONS$. Calculated MR 82.65
Found %: P 10.82; 10.81
$C_{13}H_{30}PONS$. Calculated%: P 11.10

The yield of ester was 1.15 g (33%).

10. O-Octyl Triethylphosphonamidothioate. The ester was prepared from 4.8 g of octyl triethylphosphonamidite and 0.59 g of flowers of sulfur. Vacuum distillation of the reaction product from an Arbuzov flask gave O-octyl triethylphosphonamidothioate, b.p. 144-144.5° (1 mm); d_4^{20} 0.9516; n_D^{20} 1.4793.

Found MR 87.45
$C_{14}H_{32}PONS$. Calculated MR 87.27
Found %: P 10.11; 10.2
$C_{14}H_{32}PONS$. Calculated%: P 10.37

The yield of ester was 1.8 g (33.4%).

11- O-Nonyl Triethylphosphonamidothioate. The ester was prepared from 4.2 g of nonyl triethylphosphonamidite and 0.49 g of flowers of sulfur. Vacuum distillation of the reaction product from an Arbuzov flask gave O-nonyl triethylphosphonamidothioate, b.p. 151-152° (1 mm); d_4^{20} 0.9495; n_D^{20} 1.4796.

Found MR 91.91
$C_{15}H_{34}PONS$. Calculated MR 91.88
Found %: P 9. 81- 9. 78
$C_{15}H_{34}PONS$. Calculated%: P 10.1

The yield of ester was 1.2 g (25.6%).

12. O-Decyl Triethylphosphonamidothioate. The ester was prepared from 4.9 g of decyl triethylphosphonamidite and 0.54 g of flowers of sulfur. Vacuum distillation of the reaction products from an Arbuzov flask gave O-decyl triethylphosphonamidothioate, b.p. 170-172° (1 mm); d_4^{20} 0.9446; n_D^{20} 1.4800.

Found MR 96.67
$C_{16}H_{36}PONS$. Calculated MR 96.51
Found%: P 9.34; 9.45
$C_{16}H_{36}PONS$. Calculated%: P 9.06

The yield of ester was 1.05 g (19.2%).

III. Action of Ethanol on Triethylphosphonamidous Chloride.

A mixture of 20 g of triethylphosphonamidous chloride and 50 ml of absolute ether was prepared in a three-necked flask fitted with stirrer, dropping funnel, and reflux condenser. The reaction flask was cooled with snow and salt, and 11 g of ethanol was added to its contents from the dropping funnel over a period of 40 minutes. The reaction was carried out in a current of carbon dioxide. As the alcohol was added, a precipitate formed. It was filtered off at the pump, and the residue, after removal of ether, was vacuum-distilled from an Arbuzov flask, when the following fractions were obtained:

Fraction I	b.p. to 55° (32 mm);	0. 9 g
Fraction II	b.p. 55-60° (32 mm);	14.1 g
Residue		0.8 g

Redistillation of Fraction II yielded:

Fraction I	b.p. to 55° (32 mm);	0.47 g
Fraction II	b.p. 55-56° (32 mm);	10.5 g
Fraction III	b.p. 56-61° (32-33 mm);	2.7 g

The analysis and constants of Fraction II, b.p. 55-56° (32 mm), showed that it was diethyl ethylphosphonite, d_4^{20} 0.9200; n_D^{20} 1.4215.

Found MR 41.44
$C_6H_{15}PO_2$. Calculated MR 41.39
Found %: P 20.73; 20.88
$C_6H_{15}PO_2$. Calculated %: P 20.65

The crystalline substance was recrystallized twice from alcohol. It was found to be diethylamine hydrochloride (confirmed by analysis for chlorine).

Found %: Cl 32.28; 32.36
$C_4H_{12}NCl$. Calculated %: Cl 32.45

SUMMARY

1. Triethylphosphonamidous chloride and alkyl triethylphosphonamidites (ranging from the methyl to the decyl ester) were synthesized.

2. Triethylphosphonamidothioic chloride was prepared by addition of sulfur to triethylphosphonamidous chloride in presence of aluminum chloride.

3. Alkyl triethylphosphonamidothioates (ranging from the methyl to the decyl ester) were prepared by addition of sulfur to alkyl triethylphosphonamidites.

4. When triethylphosphonamidous chloride was treated with an alcohol, the amido group was eliminated in the form of diethylamine hydrochloride and a dialkyl ethylphosphonite was formed.

LITERATURE CITED

[1] G. M. Koslapoff and R. M. Watson, J. Am. Chem. Soc., No. 9, 73,4101 (1951).

Received January 11,1955

A. E. Arbuzov Chemical Institute of the
Kazan Affiliated Institute of the USSR
Academy of Sciences.

PARACHORS OF TRIALKYLMETHYLSILANES

B. A. Arbuzov and V. S. Vinogradova

In the course of the use of Gibling's group-value method for the calculation of theoretical values of the parachor and the comparison of these values with the experimentally determined values of organic compounds of various types, it has been found necessary to introduce corrections into the theoretical values, these being required— according to Gibling— in order to take account of the interaction of hydrocarbon chains (corrections for parallelism) [1]. Corrections of this sort were found to be necessary for ethers [1, 2], amines [3], and arsines [4], which contain either a polar group (C = O, P = O, S = O), or atoms having unshared electrons, which can cause the bending of ether or hydrocarbon chains in the direction of the central polar group or the atom with the unshared electron pair. After being bent, the chains are arranged parallel to one another, so that a correction for parallelism is required. It would be of interest to determine whether not only compounds of this type, but also compounds of hydrocarbon character— not containing polar groups or atoms having unshared electron pairs—can require parallelism corrections.

Much attention has been given recently to the study of the parachors of hydrocarbons [5]. The value of the parachor has been found to be very sensitive with respect to the structure of a hydrocarbon molecule. Effects due to the presence of side chains and their positions in the hydrocarbon molecule are particularly notable (''strain constant'') [6]. All of the experimental results, however, refer to hydrocarbons having short side chains (methyl, ethyl), and for these it is impossible to determine whether the hydrocarbon chains interact and become parallel [5]. In order to resolve the question of corrections for parallelism, instead of hydrocarbons having long chains, such as trialkyl- and tetraalkyl-methanes, we selected the more accessible silanes of analogous structure for investigation. As the parallelism correction is more clearly manifested when three chains rather than four (when paired interactions are possible) are present in the molecule, we prepared a series of trialkylmethylsilanes for the investigation.

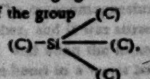
Table 1 gives the constants of the compounds that we prepared, the method of preparation being based on that already described for triethylmethylsilane [8] —reaction of trichloromethylsilane with the corresponding organomagnesium compounds.

In the literature there are data on the preparation of compounds No. 1, 2, and 3 of Table 1, but their properties have not been described fully. Compounds No. 1 and 2 were prepared by reaction of the corresponding trialkylfluorosilanes with methyl magnesium iodide the only constant given for No. 1 is b.p. 126.8° (760 mm) [9]. No. 2 is stated to have b.p. 183° (765 mm) and $n_D^{16.5}$ 1.4290, the analytical data being: found % C 69.5; H 14.1; Calculated %: C 69.7; H 14.05 [9]. Tributylmethylsilane (No. 3) was prepared by the action of C_4H_9Li on triethylmethylsilane, and its boiling point is given as 101-104° (9mm) [10].

Data in the literature on the calculation of the parachors of aliphatic hydrocarbons indicate the necessity of making corrections to the values of the molecular parachor for the interaction of side chains, but different corrections are proposed by different investigators. The ''strain constant'' of Mumford and Phillips is about 3 units for each side chain, and it varies according to the structure of the molecule and the length of the side chain. Gibling finds a correction of − 1.7 units for 2,3-dimethylpentane and for 3,4-dimethylhexane and a correction of − 1.2 units for 3-ethylpentane [11]. Quayle finds corrections varying from − 2.1 to − 6.5 units for 17 octane isomers, and in calculations he assumes an average value of − 3.7 units for each branching [5].

Table 2 gives values of parachors determined by us for a series of trialkylmethylsilane, beginning from triethylmethylsilane and continuing to tridecylmethylsilane, in which the branching chains are much longer.

The atomic parachors of silicon given in the literature were calculated from the parachors of tetraalkylsilanes [12] and compounds of other classes, and they have nonidentical values ranging from 25.8 to 38.2 units [13]. From the parachor of triethylmethylsilane we have calculated the parachor of the group



to be 33.38 units.

The theoretical values of the parachors were calculated by the ''group-value method'' both with allowance for the possibility of side-chain interaction (I-between three chains, II- between two chains), and also without such allowance. In the latter case the discrepancy between observed and calculated parachors exceeded experimental error (it varied from − 0.3% to − 1.5%), which indicates the necessity for corrections to the value of molecular parachor to take into account the parallelism of the chains after the bend at the γ-carbon atom (the correction for the γ-carbon of each chain is − 1.4 units) [14].

The best agreement between observed and calculated parachors was obtained when it was assumed that interaction occurred between two chains of the molecule rather than three, for which considerable discrepancies were observed (from + 0.3% to + 2.1%) (Table 2). The data in Table 2 enable us to conclude that for trialkylmethylsilane molecules the most probable structure is an extended one in which two chains are parallel, which is in accord with data on parachors obtained previously for esters of orthopropionic and various other acids [15], in which the central atom is not polar.

Quayle [5] has recently proposed that the calculation be based on atomic parachors, and he calculated the parachor of the CH_2 group to be 40.0 units for $\underline{n} < 12$ and 40.3 units for $\underline{n} < 12$. The parachors of trialkylmethylsilanes calculated from Quayle's atomic parachors with a correction for two branchings in the molecule ($-3.7 \times 2 = -7.4$ units) differ appreciably from the observed values, the difference being + 2.5% for triethylmethylsilane, + 1.3% for methyltripropylsilane, still less at + 0.1% for tributylmethylsilane, and then becoming negative until it attains − 0.9 unit for tridecylmethylsilane. Better agreement is therefore obtained between observed and calculated parachors when these are calculated by the group-value method rather than by Quayle's method of atomic parachors.

EXPERIMENTAL

Trialkylmethylsilanes were prepared by the general method of reaction of trichloromethylsilane with the corresponding organomagnesium bromides.

Triethylmethylsilane. Ethylmagnesium bromide was prepared from 16.5 g of magnesium and 75 g of ethyl bromide (added dropwise) in 250 ml of dry ether. The solution so obtained was stirred, and 20 g of trichloromethylsilane, b.p. 66°, was added gradually. Reaction was very vigorous. When the whole of the trichloromethylsilane had been added, the mixture was heated under reflux in a water bath for three hours. Ether was distilled off, and the residue was heated for a further three hours and then decomposed with 10% hydrochloric acid. The acid was added dropwise with the reflux condenser still in place. A little ether was added to the reaction product, and the resulting ethereal solution was washed, first with water, then with sodium carbonate solution, and finally with water again; it was dried over calcium chloride. The ether was distilled off, and the distillation of the residue yielded 6 g of triethylmethylsilane, b.p. 123.0 − 124.0° (760 mm). After redistillation over metallic sodium, the trimethylsilane had b.p. 123-124° (760 mm); n_D^{20} 1.4130, d_4^{20} 0.7420, Found MR 43.78; Calculated MR 44.17 γ^{20} 20.82.

Methyltripropylsilane. This was prepared similarly to triethylmethylsilane. Propylmagnesium bromide was prepared in 250 ml of dry ether from 13 g of magnesium and 65 g of propyl bromide, and 20 g of trichloromethylsilane was added immediately to the resulting solution. Reaction began when the mixture was heated in a water bath. The mixture was heated for three hours, and the residue remaining after removal of ether was heated for six hours. Dilute hydrochloric acid was added under ice cooling. The washed and dried product distilled completely (7 g) through a Widmer column at 177-181° (760 mm). After redistillation over sodium the methyltripropylsilane had b.p. 182.5 - 183.5° (765 mm); n_D^{20} 1.4280; d_4^{20} 0.7660; Found MR 57.88; Calculated MR 58.06; γ^{20} 22.90.

In view of their high stabilities, the trialkylmethylsilanes were analyzed by the combustion method. The weighed sample in the boat was covered with a finely ground mixture of cupric oxide and lead chromate, and part of the cupric oxide in the combustion tube was replaced by lead chromate, which was contained in a cartridge of copper gauze. Combustion of trialkylmethylsilanes without the use of lead chromate evidently led to the formation of carbides that could not be broken down by heat [16], and the carbon results for methyltripropylsilane, methyltrioctylsilane, and tridecylmethylsilane were low by 1.5-3.5%, in all analyses, whereas, good agreement was obtained for hydrogen.

Found %: C 69.73; H 14.11

$C_{10}H_{24}Si$. Calculated %: C 69.72; H 14.04

Tributylmethylsilane. This was prepared in a similar way. The organomagnesium compound was prepared from 10.7 g of magnesium and 60 g of butyl bromide in 180 ml of dry ether, and it was stirred while 20 g of trichloromethylsilane was added rapidly. Reaction occurred with evolution of heat, and when the mixture was heated a precipitate formed. Ether was distilled off, and the residue was heated for five hours in a water bath. The solid precipitate was decomposed with 10% hydrochloric acid, snow cooling being applied. The product was washed with water and sodium carbonate solution, a little ether was added, and the ethereal solution was washed with water and dried with calcium chloride. The ether was driven off, and the residue was treated with sulfuric acid, washed, diluted with ether, and dried with calcium chloride. The sulfuric acid layer was diluted with water and extracted with ether, and the ether extract was washed and dried over calcium chloride. Vacuum distillation yielded the fractions:

Fraction I b.p. 64-66° (6.5 mm); 4 g
Fraction II b.p. 92.5 - 93.5° (5 mm); 13 g

Redistillation of the higher fraction yielded tributylmethylsilane, b.p. 117-118° (17 mm); n_D^{20} 1.4375, d_4^{20} 0.7818, Found MR 71.92; Calculated MR 71.95; γ^{20} 24.53.

Found %: C 72.74; H 14.11
$C_{13}H_{30}Si$. Calculated %: C 72.81; H 14.10

Trihexylmethylsilane. Trihexylmethylsilane has not been described in the literature. Hexylmagnesium bromide was prepared in 150 ml of dry ether from 7.5 g of magnesium and 50 g of hexyl bromide, b.p. 46-47° (13 mm)(added dropwise). To the resulting solution 10 g of trichloromethylsilane was added dropwise. The mixture was heated in a water bath for 90 minutes. A precipitate formed on standing. The ether was distilled off, and the precipitate was heated for 5 hours 30 minutes and then cautiously decomposed with 10% hydrochloric acid, which was added dropwise with the reflux condenser in position. The product was washed with water and sodium carbonate solution, and ether was then added. The ethereal solution was washed with water and dried over calcium chloride. The ether was distilled off, and vacuum distillation of the residue through a small Widmer column gave the fractions:

Fraction I b.p. 105-172.5° (8 mm)
Fraction II b.p. 172.5-174° (8 mm) (not corrected) – 12.5 g

A second distillation with an Anschütz thermometer yielded a product having b.p. 176.5-177° (9 mm); n_D^{20} 1.4465 d_4^{20} 0.8016; Found MR 99.41; Calculated MR 99.73; γ^{20} 26.75.

Found %: C 76.56; H 14.19
$C_{19}H_{42}Si$. Calculated %: C 76.43; H 14.18

Methyltrioctylsilane. Methyltrioctylsilane has not been described in the literature. Octylmagnesium bromide was prepared from 65 g of octyl bromide and 8 g of magnesium, and to the resulting solution 12 g of trichloromethylsilane was added. Reaction did not begin immediately. A precipitate formed when the mixture was heated for three hours in a water bath. The ether was distilled off, and the residue was heated for eight hours. The reaction product was treated as described above. Much frothing occurred during vacuum distillation. After many fractionations through a small Widmer column, the following fractions were obtained:

Fraction I b.p. 137-141° (4.5 mm); 4 g
Fraction II b.p. 205-210° (3 mm); 14.5 g

Redistillation of the higher fraction gave a substance having b.p. 209.5-211° (5 mm); n_D^{20} 1.4520; d_4^{20} 0.8128; Found MR 127.27; Calculated MR 217.51; γ^{20} 28.35.

Found %: C 78.05; H 14.13
$C_{25}H_{54}Si$. Calculated %: C 78.45; H 14.22

Tridecylmethylsilane. Tridecylmethylsilane has not been described in the literature. Decylmagnesium bromide was prepared from 66 g of decyl bromide and 7.2 g of magnesium in dry ether, and to the resulting solution 10 g of trichloromethylsilane was added. Reaction occurred without rise in temperature. A precipitate formed when the mixture was heated for three hours in a water bath. After the ether had been removed, the mixture was heated for a further eight hours. The product was decomposed and then treated as described above. Distillation from an Arbuzov flask gave the fractions:

Fraction I b.p. up to 187° (3 mm)
Fraction II b.p. up to 187-215° (3 mm)
Fraction III b.p. up to 215-230° (3 mm)

Fractionation of the fraction boiling up to 187° (3 mm) through a Widmer column gave 6 g of decane, b.p. 62-63°

TABLE 1

No.	Formula	B.p. (°C)	Pressure (mm)	n_D^{20}	d_4^{20}	MR		γ^{20}
						Found	Calculated*	
1	$(C_2H_5)_3SiCH_3$**	123-124	(760)	1.4130	0.7420	43.78	44.17	20.82
2	$(n\text{-}C_3H_7)_3SiCH_3$	182.5-183.5	(765)	1.4280	0.7660	57.88	58.06	22.90
3	$(n\text{-}C_4H_9)_3SiCH_3$	117-118	(17)	1.4375	0.7818	71.92	71.95	24.53
4	$(n\text{-}C_6H_{13})_3SiCH_3$	176.5-177	(9)	1.4465	0.8016	99.41	99.73	26.75
5	$(C_8H_{17})_3SiCH_3$	209.5-211	(5)	1.4520	0.8128	127.27	127.51	28.35
6	$(C_{10}H_{21})_3SiCH_3$	261-262.5	(4.5)	1.4565	0.8211	155.0	155.29	29.70

---

* The molecular refraction was calculated from bond values. The refraction of the C–Si bond was taken as 2.5 units [7].

** Data in the literature b.p. 127° (760 mm), n_D^{20} 1.4160; d_{20}^{20} 0.7437, MR Found 43.96.

TABLE 2

No.	Formula of Compound	P		Correction made	Discrepancy (%)
		Found	Calculated		
1	$(C_2H_5)_3SiCH_3$	374.9	–	–	–
2	$(n\text{-}C_3H_7)_3SiCH_3$	492.2	491.1	3γ − 4.2	+ 0.2
3	$(n\text{-}C_4H_9)_3SiCH_3$	610.3	I 605.2	3γ 3∥ − 10.8	+ 0.8
			II 609.7	3γ 3∥ − 6.4	+ 0.1
4	$(C_6H_{13})_3SiCH_3$	847.1	I 834.1	3γ 9∥ − 24.0	+ 1.5
			II 847.5	3γ 3∥ − 10.8	0
5	$(C_8H_{17})_3SiCH_3$	1086.7	I 1064.2	3γ 15∥ − 37.2	+ 2.1
			II 1086.6	3γ 5∥ − 15.2	0
6	$(C_{10}H_{21})_3SiCH_3$	1322.0	I 1316.3	3γ 21∥ − 50.4	+ 0.4
			II 1326.8	3γ 7∥ − 19.6	− 0.3

(15 mm); n_D^{20} 1.4130. Several fractionations of the higher fractions yielded 12 g of a substance having b.p. 261-262.5° (4.5 mm); n_D^{20} 1.4565; d_4^{20} 0.8211; Found MR 155.0; Calculated MR 155.29; γ^{20} 29.70.

It was not found possible to distil tridecylmethylsilane from a flask fitted with a small Widmer column. The substance distilled only when it was very much overheated (it flowed over the walls in a continuous film).

Found %: C 79.89; H 14.44

$C_{31}H_{66}Si$. Calculated %: C 80.08; 14.31

SUMMARY

1. Trihexylmethyl-, methyltrioctyl-, and tridecylmethyl-silanes, which have not been described previously in the literature, were synthesized.

2. Parachors were determined for 2 series of trialkylmethylsilanes, ranging from triethyl- to tridecyl-methyl-silanes.

3. The parachor data indicate that trialkylmethylsilanes probably have extended structures in which two chains lie parallel, similar to the structure (also derived from parachor data) of orthopropionic esters, in which there is also an absence of any kind of polarity in the central atom.

LITERATURE CITED

[1] T. W. Gibling, J. Chem. Soc., 1944, 380.

[2] B. A. Arbuzov and V. S. Vinogradova, Bull. Acad. Sci., USSR, Div. Chem. Sci., 1951, No. 6 733, J. Phys Chem. 22, 303 (1948); Proc. Acad. Sci., USSR, 60, 779 (1948); V. S. Vinogradova, Sci. Memoirs Kazan State Univ. 110, (9), 1950, p. 5.

[3] B. A. Arbuzov and L. M. Guzhavina, Proc. Acad. Sci., USSR, 61, 63 (1948); B. A. Arbuzov and L. M. Kataeva, J. Phys. Chem. 26, 1298 (1952).

[4] K. I. Kuzmin and G. Kamai, Collection of Papers on General Chemistry, Acad. Sci., USSR Press, Moscow and Leningrad, 1953, I, 223-228.

[5] O. R. Quayle, Chem. Rev., 53, 439 (1953).

[6] S. A. Mumford, J. W. C. Phillips, J. Chem. Soc., 1929, 2112.

[7] E. L. Warrick, J. Am. Chem. Soc., 68, 2455 (1946).

[8] F. C. Whitmore, L. H. Sommer, P. A. DiGiorgio, W. A. Strong, J. Am. Chem. Soc., 68, 475 (1946).

[9] C. Eaborn, J. Chem. Soc., 1949, 2755.

[10] Larsson van Gilse van der Pals, Chem. Abs., 1952, 2516.

[11] T. W. Gibling, J. Chem. Soc., 1945, 239.

[12] W. J. Jones, L. H. Thomas, E. H. Pritchard, S. T. Bowden, J. Chem. Soc., (1946), 824.

[13] H. Gilman and G. E. Dunn, Chem. Rev., 52, 81 (1953).

[14] B. A. Arbuzov and V. S. Vinogradova, Proc. Acad. Sci., USSR, 60, 779, (1948).

[15] B. A. Arbuzov and E. K. Yuldasheva, Proc. Acad. Sci., USSR, 70, 231 (1950).

[16] K. A. Andrianov and M. V. Sobolevsky, Macromolecular Organosilicon Compounds, p. 310, Defense Press 1949.

Received December 22, 1954

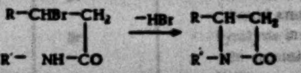
A. M. Butlerov Chemical Institute of the
V. I. Ulyanov-Lenin State University, Kazan

NEW METHOD OF PREPARING β-LACTAMS *

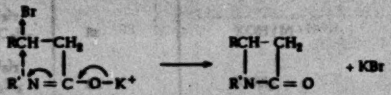
I. L. Knunyants and N. P. Gambaryan

When it had been established that penicillin contains a condensed thiazolidine β-lactam system, various syntheses of lactams of β-amino acids followed. The previously known methods for the preparation of β-lactams – addition of ketones to imines [1-7] or to aromatic nitroso compounds [8], reaction of esters of β-bromo carboxylic acids with imines in presence of zinc [6, 9], and cyclization of β-amino acids, or of their acyl derivatives or esters [6, 10-12] – have been recently supplemented by several new methods: condensation of double acylated aminoacetyl chlorides with various imines and thiazolines [13-18], cyclization of α-haloacyl derivatives of aminomalonic ester in presence of bases [19, 20], and condensation of diazomethane with aryl isocyanates [21, 22].

All of these methods give only limited possibilities for the synthesis of β-lactams, since the ranges of applicability of these reactions are narrow and the starting compounds are generally not readily available. The possibility was not excluded theoretically of the formation of the four-membered β-lactam ring by the action of alkalis on amides of β-halo carboxylic acids:



However, elimination of hydrogen halide by the action of alcoholic alkali, by sodamide suspended in absolute ether, by liquid ammonia, and by thermal treatment always yielded amides of the corresponding unsaturated acids (see Tables 1 and 5). It is evident that nucleophilic attack at the β-carbon atom does not occur owing to insufficient electron density on the amide nitrogen atom. The desired course of reaction, therefore, could be ensured only by the selection of the reactants and reaction conditions so that the electron density of the nitrogen atom would be greatly increased. It was natural to make use of solutions of alkali metals or amides of alkali metals in liquid ammonia. Under these conditions the acidity of the amide will be increased and the salt of its imine form will be stabilized. The formation of a salt of this kind should result in a considerable increase in the electron density of the nitrogen atom. In this way the necessary conditions will be created for an attack on the electrophilic β-carbon atom by the nitrogen atom carrying the unshared pair of electrons:



The experimental results were fully in accord with our expectations. When β-chloro- or β-bromo-hydrocinnamanilide was treated with a solution of potassium in liquid ammonia, both hydrocinnamanilide and 1,4-diphenyl-2-azetidinone were formed in good yield. The best results were obtained by the use of solutions of sodamide or potassium in liquid ammonia, the yields of 1,4-diphenyl-2-azetidinone being then almost quantitative.

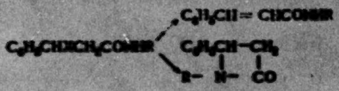
The investigations showed that the result of the reaction is almost independent of the substituent in the amino group and that amides of β-bromohydrocinnamic acid give higher yields than those of β-chlorohydrocinnamic acid (Table 1).

In this way we succeeded in preparing a series of new N-substituted azetidinones, in which the nitrogen carries not only simple radicals, but also residues of saturated and unsaturated acids:

---

* This paper is publised under the regulations governing "Brief Communications".

TABLE 1



$$C_6H_5CHXCH_2CONHR \rightarrow \begin{cases} C_6H_5CH=CHCONHR \\ \begin{array}{ccc} C_6H_5CH & - & CH_2 \\ \vert & & \vert \\ R-N & - & CO \end{array} \end{cases}$$

No.	R	X	Reaction conditions	Yield of $C_6H_5CH=CHCONH$ $\vert$ R (%)	Yield of $C_6H_5CH-CH_2$ $\vert$ $R-N-CO$ (%)
1	C_6H_5	Cl	KNH_2	–	85•
2	C_6H_5	Cl	$NaNH_2$	–	75
3	C_6H_5	Cl	Solution of potassium in liquid ammonia	–	45••
4	C_6H_5	Cl	Liquid ammonia (a)	74•••	–
5	C_6H_5	Cl	KOH (b)	60	–
6	C_6H_5	Cl	3 hours; suspension of sodamide in benzene	35	–
7	C_6H_5	Br	KNH_2	–	94
8	C_6H_5	Br	$NaNH_2$	–	90
9	C_6H_5	Br	Solution of potassium in liquid ammonia	–	63••••
10	C_6H_5	Br	Pyrolysis at 140-150° ; 20-minutes	45	–
11	C_6H_{11}	Cl	KNH_2	12.8	80
12	C_6H_{11}	Cl	$NaNH_2$	11.7	78
13	C_6H_{11}	Cl	NaOH (b)	88	–
14	$CH_2C_6H_5$	Cl	KNH_2	35	65
15	$CH_2C_6H_5$	Cl	KOH (b)	85	–
16	$CH_2C_6H_5$	Br	KNH_2	5	88
17	$CH_2CO_2C_2H_5$	Cl	4 days; KNH_2	77•••••	2
18	$CH_2CO_2C_2H_5$	Br	4 days; KNH_2	29	37•••••
19	$CHCO_2C_2H_5$ $\vert$ $CH(CH_3)_2$	Br	KNH_2	11	60
20	$CHCO_2C_2H_5$ $\vert$ $CH(CH_3)_2$	Br	Liquid ammonia (a)	86	–
21	$CHCO_2C_2H_5$ $\vert$ $CH(CH_3)_2$	Br	KOH (b)	89	–
22	$CCO_2C_2H_5$ $\Vert$ $C(CH_3)_2$	Cl	KNH_2	19	62
23	$CCO_2C_2H_5$ $\Vert$ $C(CH_3)_2$	Cl	3days; liquid ammonia (a)	55	–
24	$CCO_2C_2H_5$ $\Vert$ $C(CH_3)_2$	Cl	KOH (b)	73	–
25	$CCO_2C_2H_5$ $\Vert$ $C(CH_3)_2$	Br	KNH_2	5	75.5

• M.p. 154-154.5° (from alcohol. A mixture with 1,4-diphenyl-2-azetidinone prepared by the condensation of ketene with N-benzylideneaniline [1] melted at the same temperature.

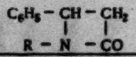
•• In addition to 1,4-diphenyl-2-azetidinone , hydrocinnamanilide was obtained in 34% yield.

••• M.p. 151° , undepressed by admixture of cinnamanilide.

•••• 1,4-Diphenyl-2-azetidinone was accompanied by hydrocinnamanilide in 18% yield.

••••• Under the conditions of the reaction the ester grouping was ammonolyzed and the corresponding amide was obtained.

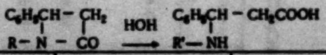
TABLE 2



$$\begin{array}{l} C_6H_5-CH-CH_2 \\ \quad\;\; | \qquad\; | \\ R-N\;-CO \end{array}$$

R	Found			Calculated			Melting point (°C)	Recrystallized from
	C	H	N	C	H	N		
C_6H_{11}	78.28	8.28	6.09	78.6	8.29	6.11	52-53	Heptane
CH_2CONH_2	64.45	5.96	13.64	64.7	5.88	13.72	144-145	Alcohol
$-CHCO_2C_2H_5$ $CH(CH_3)_2$	69.36	7.71	5.12	69.4	7.63	5.09	B.p. 167-170(1 mm)	
$-CCO_2C_2H_5$ $C(CH_3)_2$	70.38	6.78	4.93	70.33	6.96	5.12	51-52	Heptane

TABLE 3



$$\begin{array}{l} C_6H_5CH-CH_2 \qquad\qquad C_6H_5CH-CH_2COOH \\ \quad\;\; | \qquad\; | \qquad \xrightarrow{HOH} \qquad\; | \\ R-N\;-\;CO \qquad\qquad\;\; R'-NH \end{array}$$

R	R'	Reaction conditions	Found				Calculated				M.p. (°C)	Recrystallized from	Yield (%)
			C	H	N	Cl	C	H	N	Cl			
C_6H_5	C_6H_5	One hour at boil with alcoholic solution	74.7	6.29	–	–	74.6	6.23	–	–	134-135*	Ethyl acetate	83
C_6H_{11}	C_6H_{11}	Ditto	63.89	7.65	4.85	–	63.49	7.76	4.93	–	187-189***	Alcohol-ether	79
$CH_2C_6H_5$	$CH_2C_6H_5$	"	75.04	6.38	5.44	–	75.3	6.66	5.49	–	184-185**	Bicarbonate solution	90
			66.08	6.07	–	11.83	65.87	6.17	–	12.18	189-190***	–	–
CH_2CONH_2	CH_2CO_2H	4 hours at 60-70° with 2 N HCl	59.25	5.90	6.19	–	59.2	5.83	6.28	–	205-206	Water	69
$-CHCO_2C_2H_5$ $CH(CH_3)_2$	$-CHCO_2C_2H_5$ $CH(CH_3)_2$	2.5 hours at 60-70° with 2 N HCl	–	--	3.93	–	–	–	4.26	–	183-185	Alcohol	60
$-CCO_2C_2H_5$ $C(CH_3)_2$	H	1 hour at 90-95° with 20% HCl	53.23	6.05	6.91	18.32	53.59	5.98	6.95	17.67	215-217****	Alcohol-ether	80***

---

* The literature [23] gives M.p. 134°

** The literature [12] gives M.p. 187-188°

*** Isolated as the hydrochloride

**** The literature [24] gives M.p. 217-218°.

TABLE 4

$C_6H_5CHXCH_2CONHR$

R	X	Found				Calculated				M.p. (°C)	Recrystallised from	Yield (%)
		C	H	N	X	C	H	N	X			
C_6H_5	Cl	69.36	5.50	–	13.25	69.37	5.39	–	13.7	135–135.5	Alcohol	83
C_6H_5	Br	–	–	4.61	–	–	–	4.6	–	125.5–126	Ethyl acetate	85
C_6H_{11}	Cl	–	–	4.81	–	–	–	5.27	–	116–117	" "	79
$CH_2C_6H_5$	Cl	69.46	5.76	–	13.34	70.2	5.85	–	13.0	116–116.5	Alcohol	70
$CH_2C_6H_5$	Br	–	–	4.32	–	–	–	4.4	–	117–118	Ethyl acetate	75
$CH_2CO_2C_2H_5$	Cl	58.78	5.95	–	12.9	57.95	5.98	–	13.17	53–55	Petroleum ether	73
$CH_2CO_2C_2H_5$	Br	–	–	4.41	–	–	–	4.46	–	82–83	Ethyl acetate	93
$-CCO_2C_2H_5$ ‖ $C(CH_3)_2$	Cl	–	–	4.6	–	–	–	4.52	–	115–116	Alcohol	83
$-CCO_2C_2H_5$ ‖ $C(CH_3)_2$	Br	–	–	3.74	–	–	–	3.95	–	125.5–126	Ethyl acetate	70
$-CHCO_2C_2H_5$ | $CH(CH_3)_2$	Br	–	–	3.64	–	–	–	3.9	–	80–81	Heptane	87

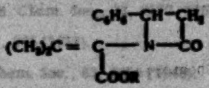
TABLE 5

$C_6H_5CH = CHCONHR$

R	Found			Calculated			M.p. (°C)	Recrystallized from
	C	H	N	C	H	N		
C_6H_{11}			5.99			6.1	172–173	Aqueous alcohol
$CH_2C_6H_5$	80.9	6.23		81.01	6.32		103–104 •	Alcohol
CH_2CONH_2	64.69	5.81	13.44	64.7	5.88	13.72	171–172	Alcohol
$-CHCO_2C_2H_5$ | $CH(CH_3)_2$			5.01			5.09	116–117	Aqueous alcohol
$-CCO_2C_2H_5$ ‖ $C(CH_3)_2$			5.12			5.12	164.5–165	Ethyl acetate
$-CCO_2CH_3$ ‖ $C(CH_3)_2$	68.67	6.68	5.39	69.5	6.56	5.4	144–145	Ethyl acetate

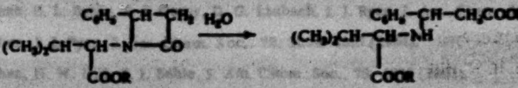
---

• For N-benzylcinnamamide the literature [23] gives m.p. 94 - 96°



The properties of the new azetidinones are given in Table 2.

The structures of the β-lactams so obtained were proved by their hydrolysis to the corresponding amino acids. The method therefore enables us to pass to β-amino acids and to difficulty accessible mixed amino acids (Table 3):



The original amides were prepared in the usual way: the action of amines on β-bromo- and β-chloro-hydrocinnamoyl chlorides*. When β-bromohydrocinnamic acid was treated with the theoretical amount of phosphorus pentachloride, the expected β-bromohydrocinnamoyl chloride was formed, but when β-bromohydrocinnamic acid was heated with excess of thionyl chloride, bromine was quantitatively replaced by chlorine and β-chlorohydrocinnamoyl chloride was formed.

EXPERIMENTAL

β-Chlorohydrocinnamoyl Chloride [1]. β-Bromohydrocinnamic acid (20 g) was boiled for two hours with thionyl chloride (30 ml). On the next day excess of thionyl chloride was distilled off, and vacuum distillation of the residue yielded 19.3 g (86%) of β-chlorohydrocinnamoyl chloride, b.p. 130-131° (14 mm).

Found %: C 52.59; H 4.01
$C_9H_8OCl_2$. Calculated %: C 53.20; H 3.94

Substituted Amides of β-Chloro- and β-Bromo-hydrocinnamic Acids. A solution of two moles of amine in absolute ether was added dropwise to a stirred ice-cooled solution of one mole of the acid chloride in absolue ether. The precipitate formed was filtered off, washed with water, and recrystallized.

General Method of Preparing β-Lactams. The appropriate β-halohydrocinnamamide (1 mole) was added to a solution of 1 mole of sodamide or potassamide; the mixture was shaken vigorously and set aside overnight. On the next day ammonia was evaporated off at room temperature, and the residue was washed with water. Liquid β-lactams were purified by vacuum distillation, and solid β-lactams were recrystallized from suitable solvents (Table 2).

N-Substituted Cinnamamides. a) An N-substituted β-halohydrocinnamamide was added to liquid ammonia, and the mixture was shaken vigorously and set aside overnight. On the next day ammonia was evaporated off at room temperature, and the residue was washed with water and recrystallized.

b) The appropriate substituted β-halohydrocinnamamide (1 mole) was added to alcoholic alkali (1 mole), and the mixture was allowed to stand for 5-20 minutes at room temperature. Water was then added, and the precipitated crystals were filtered off and recrystallized from suitable solvents (Table 5).

SUMMARY

A method has been devised for the synthesis of β-lactams from amides of β-halocarboxylic acids. Some new azetidinones with residues containing carboxyl groups on the nitrogen have been prepared. The method permits the conversion of β-amino acids into difficulty accessible mixed (secondary) amino acids.

LITERATURE CITED

[1] H. Staudinger, Ber. 50, 1035 (1917).

[2] H. Staudinger, H. W. Klever, P. Kober, Ann. 374, 1 (1910).

[3] H. Staudinger, H. W. Klever, Ber., 40, 1149 (1907).

[4] H. Staudinger, Ann. 356, 51 (1907).

[5] H. Staudinger, J. Maier, Ann. 401, 292 (1913).

[6] The Chemistry of Penicillin, Princeton, N.J., 1949, 973.

---

* The properties of the new amides are given in Tables 4 and 5.

[7] A. D. Holley, R. W. Holley, J. Am. Chem. Soc., 73, 3172 (1951).

[8] H. Staudinger, S. Lelagin, Ber. 44, 365 (1911).

[9] H. Gilman, M. Speeter, J. Am. Chem. Soc., 65, 2255 (1943).

[10] R. W. Holley, A. D. Holley, J. Am. Chem. Soc., 1949, 71, 2124.

[11] J. H. Mowat, C. A. 43, 7972 (1949).

[12] R. W. Holley, A. D. Holley, J. Am. Chem. Soc., 1949, 71, 2129 (1949).

[13] J. C. Sheehan, E. L. Buhle, E. J. Corey, D. G. Laubach, J. J. Ryan, J. Am. Chem. Soc., 72, 3828 (1950).

[14] J. C. Sheehan, J. J. Pyan, J. Am. Chem. Soc., 73. 1204. 4367 (1951).

[15] J. C. Sheehan, H. W. Hill, E. 1. Buhle, J. Am. Chem. Soc., 73, 4373 (1951).

[16] J. C. Sheehan, G. D. Laubach, J. Am. Chem. Soc., 73, 4752 (1951).

[17] J. C. Sheehan, G. D. Laubach, J. Am. Chem. Soc., 73, 4376 (1951).

[18] J. C. Sheehan, E. J. Corey, J. Am. Chem. Soc., 73, 4765 (1951).

[19] J. C. Sheehan, A. K. Bose, J. Am. Chem. Soc., 72, 5158 (1950).

[20] J. C. Sheehan, A. K. Bose, J. Am. Chem. Soc., 73, 1761 (1951).

[21] J. C. Sheehan, P. P. Izzo, J. Am. Chem. Soc., 70, 1985 (194[illegible]).

[22] J. C. Sheehan, P. P. Izzo, J. Am. Chem. Soc., 71, 4059 (1949).

[23] S. Kushner, R. I. Cassell, J. Morton, J. H. Williams, J. Org. Chem. 16. 1283 (1951).

[24] E. Fourneau, R. Billeter, Bull. Soc. Chim. 7, 593 (1940).

[25] P. Posner, Ber. 38, 2316 (1905).

Received April 20,1955

Institute of Heteroorganic Compounds
of the USSR Academy of Sciences

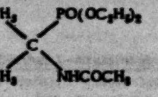
ACYLATION OF AMINOALKYLPHOSPHONIC AND AMINOALKYLPHOSPHONOTHIOIC ACID

T. Ya Medved and M. I. Kabachnik

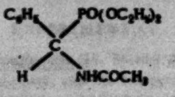
In a previous investigation we studied the acylation of aminomethylphosphonic acid [1]. We found that it is more difficult to acylate than its carboxylic analog, glycine. It was considered to be of interest to investigate the acylation of other aminoalkylphosphonic acids and their esters. Moreover, we required N-acyl derivatives of aminoalkylphosphonic acids as starting materials in other investigations.

As we had readily accessible methods at our disposal for the preparation of aminoalkylphosphonic [2] and aminoalkylphosphonothioic [3] acids and their esters, we investigated the acetylation and benzoylation of these compounds. We found that reaction of aminoalkylphosphonic esters with excess of acetic anhydride yielded the corresponding N-acetyl derivatives. Reaction was vigorous: when acetic anhydride was added to an aminoalkylphosphonic ester, the temperature of the reaction mixture rose rapidly to 50-70° and the process was practically complete in 30-40 minutes. When the excess of acetic anhydride was distilled off, the residue usually solidified rapidly, and it was sufficient to recrystallize it once only in order to obtain a pure substance.

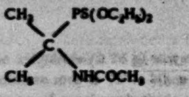
Reactions with acetic anhydride yielded diethyl 1-acetamido-1-methylethylphosphonate (I), m.p. 96-97°, and diethyl α-acetamidobenzylphosphonate (II), m.p. 144°. The acylation of an aminoalkylphosphonothioic ester with acetic anhydride proceeded similarly; we prepared O,O-diethyl 1-acetamido-1-methylethylphosphonothioate (III), a colorless substance, b.p. 128-129° (3 mm), which readily solidifies at room temperature and will then melt at 47-48°.



(I)



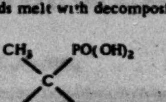
(II)



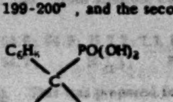
(III)

In order to prepare acetyl derivatives of free aminoalkylphosphonic acids by reaction with acetic anhydride it was necessary to heat the reaction mixture under reflux in a boiling water bath for 1-2 hours. When excess of acetic anhydride was distilled from the reaction mixture, the residue rapidly solidified, and the acetyl derivative so obtained could be readily recrystallized.

Reactions with acetic anhydride yielded 1-acetamido-1-methylethylphosphonic acid (IV) and α-acetamidobenzylphosphonic acid (V). Both acids melt with decomposition — the first at 199-200°, and the second at 188°.

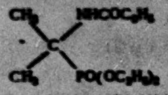


(IV)

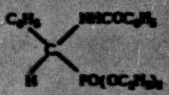


(V)

Reaction of aminoalkylphosphonic esters with benzoyl chloride yielded the corresponding N-benzoyl compounds. The reaction was carried out in presence of pyridine, and benzene was used as solvent. Benzoylation of diethyl 1-amino-1-methylethylphosphonate yielded diethyl 1-benzamido-1-methylethylphosphonate (VI), decomposition temperature 105-106°, and reaction with diethyl α-aminobenzylphosphonate yielded diethyl α-benzamidobenzylphosphonate (VII), m. p. 107°.

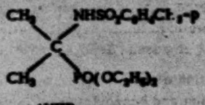


(VI)

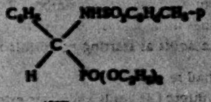


(VII)

It was found that reaction with p-toluenesulfonyl chloride could be effected in the same way as reaction with benzoyl chloride. Treatment of diethyl 1-amino-1-methylethylphosphonate with p-toluenesulfonyl chloride yielded diethyl 1-methyl-1-p-toluenesulfonamidobenzylphosphonate (VIII), a colorless substance, m.p. 121-123°. Reaction with diethyl α-aminobenzylphosphonate gave diethyl α-p-toluenesulfonamidobenzylphosphonate (IX), a crystalline substance, m.p. 127°:

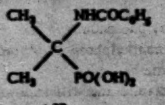


(VIII)

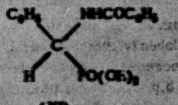


(IX)

Reaction of benzoyl chloride with free amino acids proceeds most satisfactorily in aqueous alkaline solution under Schotten-Baumann conditions. By this method we obtained 1-benzamido-1-methylethylphosphonic acid (X) and α-benzamidobenzylphosphonic acid (XI):



(X)



(XI)

EXPERIMENTAL

Diethyl 1-Acetamido-1-methylethylphosphonate (I). Freshly distilled acetic anhydride (0.76 g) was added to 0.97 of diethyl 1-amino-1-methylethylphosphonate, and the temperature of the mixture rose to 70°. When the temperature fell, the mixture was heated in a boiling water bath for 15 minutes. Excess of acetic anhydride was distilled off under reduced pressure, and the residue in the flask solidified. Recrystallization of the substance from petroleum ether gave 0.74 g (82%) of colorless crystals, m.p. 96-97°.

Found %: C 45.7; 45.5; H 8.5; 8.5; N 6.1; P 13.1; 12.8

$C_9H_{20}NPO_4$. Calculated %: C 45.6; H 8.5; N 5.9; P 13.1

Diethyl α-Acetamidobenzylphosphonate (II). Reaction of 1.22 g of diethyl α-aminobenzylphosphonate with 0.76 g of acetic anhydride gave 0.9 g (63%) of colorless crystals, m.p. 146° (from absolute ethanol).

Found %: C 54.6; 54.9; H 7.2; 7.1; P 10.8; 10.8

$C_{13}H_{20}NPO_4$. Calculated %: C 54.7; H 7.1; P 10.9

O,O-Diethyl 1-Acetamido-1-methylethylphosphonothioate (III). This was prepared from 3.15 g of O,O-diethyl 1-amino-1-methylethylphosphonothioate and 2.28 g of acetic anhydride. Excess of acetic anhydride was removed by distillation at the water pump, and the residue of the reaction mixture was vacuum-distilled from a pear-shaped Claisen flask. A second distillation gave 2.5 g (66%) of a substance having b.p. 116-11 ° (2 mm) and m.p. 47-48°. This substance has an unpleasant odor; it is soluble in organic solvents, but insoluble in water.

Found %: C 42.9; 42.5; H 8.1; 7.9; S 12.3; 12.9; P 12.3; 12.5; N 5.4; 5.5

$C_9H_{20}NPO_3S$. Calculated %: C 42.7; H 7.9; S 12.7; P 12.2; N 5.5

1-Acetamido-1-methylethylphosphonic Acid (IV). A mixture of 3.14 g of 1-amino-1-methylethylphosphonic acid (monohydrate, m.p. 256°) and 15 g of acetic anhydride was heated in a flask under reflux in a boiling water bath until the precipitate present dissolved completely. Acetic anhydride was distilled off under reduced pressure, and the solid residue was recrystallized from methanol, yielding 2.8 g (78%) of colorless crystals, m.p. 199-200°.

Found %: C 33.3; 33.2; H 6.8; 6.6; N 7.7; 7.5; P 17.0; 17.1
$C_5H_{12}NPO_4$. Calculated %: C 33.1; H 6.7; N 7.7; P 17.1

α-Acetamidobenzylphosphonic Acid (V). The acid (V) was prepared from 1.87 g of α-aminobenzylphosphonic acid and 10 g of acetic anhydride. The procedure was the same as for the acid (IV). Recrystallization from a mixture of methanol and ether gave 1.4 g (60%) of a colorless crystalline substance, m.p. 186°.

Found %: C 46.8; 46.9; H 5.8; 5.9; N 6.5; 6.4; P 13.6; 13.7
$C_9H_{12}NPO_4$. Calculated %: C 47.2; H 5.3; N 6.1; P 13.5

Diethyl 1-Benzamido-1-methylethylphosphonate (VI). Benzoyl chloride (1.5 g) was added dropwise to a mixture of 1.5 g of diethyl 1-amino-1-methylethylphosphonate, 15 ml of pyridine, and 30 ml of benzene. The resulting mixture was heated for 30 minutes in a bath at 60-70°, and crystals of pyridine hydrochloride were gradually precipitated on the walls of the flask. When cool the mixture was poured into 300 ml of water. the benzene layer wa separated, and the aqueous layer was extracted with 30 ml of benzene. The combined benzene solution was washed with 5% solution of sodium carbonate and dried over sodium sulfate. The benzene was then distilled off, and petroleum ether was added to the residue. The crystals which then precipitated were separated from the solution and recrystallized from absolute ethanol. The product was 1.5 g (65%) of a colorless crystalline substance, m.p. 106°.

Found %: C 55.9; 55.9; H 7.2; 7.2; N 4.7; 4.8; P 10.4; 10.5
$C_{14}H_{22}NPO_4$. Calculated %: C 56.2; H 7.4; N 4.7; P 10.3

Diethyl α-Benzamidobenzylphosphonate (VII). The substances taken were diethyl α-aminobenzylphosphonate (1.5 g), pyridine (15 ml), benzene (30 ml), and benzoyl chloride (1.5 g). The treatment of the reaction mixture was as in the preceding experiment. The product was recrystallized from a mixture of benzene and petroleum ether, and 2 g (93.5%) of a colorless crystalline substance, m.p. 107°, was obtained.

Found %: C 62.1; 62.3; H 6.2; 6.3; N 4.2; 4.1; P 9.0; 9.1
$C_{18}H_{22}NPO_4$. Calculated %: C 62.2; H 6.3; N 4.0; P 8.9

Diethyl 1-Methyl-1-p-toluenesulfonamidoethylphosphonate (VIII). The substances taken were diethyl 1-amino-1-methylethylphosphonate (1.5 g), pyridine (15 ml), benzene (30 ml), and p-toluenesulfonyl chloride (2.5 g). The treatment of the reaction mixture was as in the first experiment. After removal of benzene there remained a brown oily liquid, which solidified when allowed to stand in a desiccator. The product was recrystallized from water, and 0.5 g (13%) of colorless crystals, m.p. 121-123°, was obtained.

Found %: C 48.0; 48.2; H 6.8; 7.0; S 8.9; 9.1; P 8.8; 8.9
$C_{14}H_{24}NPSO_5$. Calculated %: C 48.1; H 6.9; S 9.2. P 8.9

Diethyl α-p-toluenesulfonamidobenzylphosphonate (IX). The substances taken were diethyl α-aminobenzylphosphonate (1.2 g), pyridine (15 ml), benzene (30 ml), and p-toluenesulfonyl chloride (1.5 g). The procedure was as in the preceding experiment. After the benzene had been distilled off, the residue solidified. Recrystallization from 95% alcohol gave 1.5 g (76%) of colorless crystals, m.p. 127°.

Found %: N 3.5; 3.4; P 7.8; 8.0
$C_{18}H_{24}NPSO_5$. Calculated %: N 3.5; P 7.8

1-Benzamido-1-methylethylphosphonic Acid (X). A solution of 3 g of 1-amino-1-methylethylphosphonic acid in 30 ml of 10% caustic soda solution was stirred and cooled with ice water while 4 g of benzoyl chloride was added gradually at 5-7°. When addition was complete, stirring was continued at the same temperature for about one hour, and then at room temperature for a further period of one hour. The reaction mixture was then cooled with ice water, and concentrated hydrochloric acid was added gradually until the mixture was acid to Congo red. The precipitate that then formed was filtered off, and the filtrate was evaporated under reduced pressure. The precipitate obtained when the mixture was acidified was combined with the residue obtained by the evaporation of the filtrate, and the mixture was dried over calcium chloride, extracted with ether to remove benzoic acid, and then extracted with hot 96% alcohol. Evaporation of the alcoholic solution yielded 2 g (38%) of a colorless crystalline substance, m.p. 197°. From the alcohol-insoluble residue, 0.5 g of unchanged aminoalkylphosphonic acid was isolated.

Found %: C 49.5; 49.2; H 5.9; 5.9; N 5.8; 5.6; P 12.6; 12.6
$C_{10}H_{14}PNO_4$. Calculated %: C 49.4; H 5.8; N 5.8; P 12.7

α-Benzamidobenzylphosphonic Acid (XI). The substances taken were α-aminobenzylphosphonic acid (3 g), caustic potash (3.6 g made to 25 ml with water), and benzoyl chloride (3 g) The procedure was as in the previous experiment. Recrystallization from water yielded 3 g (64%) of a colorless crystalline substance, m.p. 105-107°. The substance was obtained as the monohydrate.

Found %: C 54.4; 54.5; H 5.1; 5.1; N 4.3; 4.4; P 10.2; 10.1

$C_{14}H_{14}NPO_4 \cdot H_2O$. Calculated %: C 54.5; H 5.2; N 4.5; P 10.0

SUMMARY

1. The acylation of aminoalkylphosphonic acids and their esters was investigated. It was shown that they can be acetylated by heating them with acetic anhydride; the free amino phosphonic acids require the more severe conditions.

2. It was shown that aminoalkylphosphonic esters can be benzoylated by heating them with benzoyl chloride in presence of pyridine, and that free aminoalkylphosphonic acids can be benzoylated under Schotten-Baumann conditions.

3. Aminoalkylphosphonic esters react with p-toluenesulfonyl chloride in presence of pyridine with formation of the corresponding p-toluenesulfonyl derivatives.

4. N-Acetyl, N-benzoyl, and N-p-toluenesulfonyl derivatives of aminoalkylphosphonic and aminoalkylphosphonothioic acids and esters were synthesized and characterized.

LITERATURE CITED

[1] M. I. Kabachnik and T. Ya. Medved, Bull. Acad. Sci., USSR, Div. Chem. Sci., 1953, No. 6, 1126 (T.p. 999)*.

[2] M. I. Kabachnik and T. Ya. Medved, Bull. Acad. Sci., USSR, Div. Chem. Sci., 1953, No. 5, 868 (T.p. 769)*. T. Ya. Medved and M. I. Kabachnik, Bull. Acad. Sci., USSR, Div. Chem. Sci., 1954, No. 2, 314 (T.p. 281)*

[3] M. I. Kabachnik, T. Ya. Medved and T. A. Mastryukova, Proc. Acad. Sci., USSR, 1953, No. 5, 92.

Received January 18, 1955

Institute of Heteroorganic Compounds
of the USSR Academy of Sciences

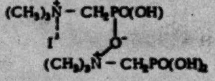
---

* T.p. = C. B. Translation pagination

METHYLATION OF 1-AMINOALKYLPHOSPHONIC ACIDS AND THEIR ESTERS

T.Ya. Medved and M.I. Kabachnik

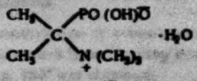
We have shown that the amino group of 1-aminoalkylphosphonic acids behaves similarly to the amino group of amino carboxylic acids in various reactions [1]. In particular, it was found [2] that N-alkylation occurs when aminomethylphosphonic acid reacts with dialkyl sulfates in an alkaline medium. Dimethyl sulfate reacts smoothly with aminomethylphosphonic acid with formation of the betaine analog $(CH_3)_3\overset{+}{N}CH_2PO(OH)\overline{O}$, which we termed a "phosphonobetaine". Diethyl sulfate reacts less readily with aminomethylphosphonic acid, and products of incomplete N-ethylation are formed, as well as the phosphonobetaine. We obtained interesting results in the alkylation of aminomethylphosphonic acid with methyl iodide [1]. When a mixture of these substances was heated in a sealed tube at 200-220° in presence of methanol, the phosphonobetaine iodide



$$\begin{array}{l}(CH_3)_3\overset{+}{N}-CH_2PO(OH) \\ \quad I^- \qquad\qquad O^- \\ (CH_3)_3\overset{+}{N}-CH_2PO(OH)_2\end{array}$$

was obtained in good yield, and this substance was converted quantitatively into the phosphonobetaine itself by the action of moist silver oxide. It was thought to be of interest to extend the investigation to the alkylation of other aminoalkylphosphonic acids.

Various aminoalkylphosphonic acids have become readily available as a result of our discovery of a synthesis of 1-aminoalkylphosphonic acids [3] based on reaction between dialkyl hydrogen phosphites, ammonia, and aldehydes or ketones. As new subjects for investigation, we selected 1-amino-1-methylethylphosphonic acid and its ethyl ester, and also α-aminobenzylphosphonic acid. We found that the first of these, like aminomethylphosphonic acid, is methylated in the cold by dimethyl sulfate in weakly alkaline solution, the main reaction product being the corresponding betaine (I):

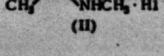


(I)

This substance was obtained as colorless crystals of the monohydrate from aqueous alcohol; it melted at 230-231°. It was readily soluble in water, and it titrated as a monobasic acid in presence of alizarin or thymolphthalein as indicator.

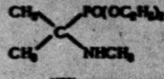
An attempt to obtain the same substance by heating 1-amino-1-methylethylphosphonic acid with methyl iodide and methanol in sealed tubes was not successful. When the mixture was heated at 100-130°, the starting materials were recovered unchanged. At higher temperatures deamination of 1-amino-1-methylethylphosphonic acid occurred, and the main reaction product, which was isolated almost quantitatively was tetramethylammonium iodide.

When the diethyl ester of 1-amino-1-methylethylphosphonic acid was taken instead of the acid itself, reaction with methyl iodide occurred much more readily, and heat was not necessary. Thus, when a mixture of diethyl 1-amino-1-methylethylphosphonate with an equimolecular amount of methyl iodide was allowed to stand in a benzene medium for two or three days at room temperature, crystals of diethyl 1-methyl-1-methylaminoethylphosphonate hydriodide (II) began to come down:



(II)

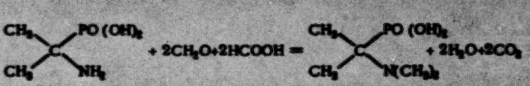
The substance is extremely hygroscopic. It can be crystallized with difficulty from absolute ethanol, and it melts with decomposition at 95°. When this salt was treated with sodium carbonate solution with simultaneous extraction of the phosphonic ester with benzene, free diethyl 1-methyl-1-methylaminoethylphosphonate (III) was obtained, after drying the extract with sodium sulfate, as a mobile liquid, b.p. 77-81° (4 mm):



(III)

When the alkylation of diethyl 1-amino-1-methylethylphosphonate was carried out under the same conditions with two molecular proportions of methyl iodide, instead of one, a mixture of substances differing in extent of methylation was formed (mono- and di-methyl derivatives), and we did not succeed in separating this mixture.

1-Amino-1-methylethylphosphonic acid can be most readily methylated with the aid of formaldehyde and formic acid. We found that, when a mixture of 1-amino-1-methylethylphosphonic acid, formaldehyde, and formic acid was heated in a boiling water bath, 1-dimethylamino-1-methylethylphosphonic acid (IV) was formed:

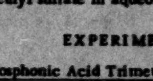


(IV)

Reaction was complete in 5-6 hours, and a yield of about 80% was obtained. The compound is a crystalline substance, and it can be recrystallized from aqueous alcohol; it melts with decomposition at 256°. It titrates as a monobasic acid when phenolphthalein is used as indicator.

Attempts to bring about the addition of methyl iodide to the above N,N-dimethyl compound with the object of obtaining a fully methylated product did not give the expected result. At temperatures of up to 130-140° the starting materials were recovered unchanged, and at still higher temperatures, the compound was deaminated. An attempt to bring about addition of methyl iodide by long shaking at room temperature of a mixture of an ethereal solution of methyl iodide and an aqueous alkaline solution of 1-amino-1-methylethylphosphonic acid was also unsuccessful.

We also carried out the methylation of α-aminobenzylphosphonic acid with formaldehyde and formic acid. Reaction was complete after 2-3 hours' heating in a water bath, and a 20% yield of α-dimethylaminobenzylphosphonic acid (V), m.p. 230° was obtained:



(V)

Thus, for the preparation of monomethyl derivatives of 1-aminoalkylphosphonic acids, reaction of their esters with methyl iodide can be used. For the preparation of dimethyl derivatives, the acids can be treated with formaldehyde and formic acid. Finally, the amino phosphonic acids can be converted into fully methylated derivatives by reaction with dimethyl sulfate in aqueous alkaline solution.

EXPERIMENTAL

1-Amino-1-methylethylphosphonic Acid Trimethylbetaine (I). A solution of 8.7 g of 1-amino-1-methylethylphosphonic acid in 75 ml of water was rendered alkaline to phenolphthalein. Dimethyl sulfate (32 g) was added slowly to the solution, and throughout the whole experiment (4-5 hours) the alkalinity of the medium was maintained. When reaction was complete, the mixture was heated in a boiling water bath for one hour, neutralized with sulfuric acid, and evaporated down on a water bath. The residue was extracted with boiling 96% alcohol. The alcohol extract was evaporated, and the residue was again extracted with alcohol. In this way the substance was freed from potassium methyl sulfate. The residue from the last extract was dissolved in a little water, dilute acid (1 : 1) was added, and the solution was boiled on a gauze for three hours in order to decompose residual methyl hydrogen sulfate. Sulfuric acid was then precipitated with barium chloride (acid medium), and the filtrate was evaporated on a water bath. The residue was again extracted with 96% alcohol, and the alcohol was evaporated from the extract. The substance remaining after removal of alcohol (the chloride of the methylated product) was dissolved in a little water, and excess of freshly precipitated silver oxide was added to the solution. The solution was heated in a water bath and filtered. Hydrogen sulfide was passed through the filtrate, silver sulfide was filtered off, and the new filtrate was evaporated on a water bath. The residue was recrystallized from aqueous alcohol (40 ml of alcohol and 15 ml of water). The crystals that came down after two days were dried in a vacuum desiccator over phosphoric oxide. The product, which was obtained as the monohydrate and amounted to 3 g (27%), melted with decomposition at 230-231°.

Found %: C 35.9; 35.9; H 9.0; 9.1; N 7.0; 7.1; P 15.5; 15.8

$C_6H_{17}NPO_3 \cdot H_2O$. Calculated %: C 36.2; H 9.1; N 7.0; P 15.6

Its aqueous solution was acid to litmus. It titrated as a monobasic acid against 0.1 N NaOH when alizarin or thymolphthalein was used as indicator:

Equivalent found: 199.0 (with alizarin)
198.0 (with thymolphthalein).
Equivalent calculated for $C_6H_{17}NPO_3 \cdot H_2O$: 199.2.

Methylation of 1-Amino-1-methylethylphosphonic Acid with Methyl Iodide. 1-Methyl-1-methylaminoethylphosphonic Acid. When 1-amino-1-methylethylphosphonic acid was heated with methyl iodide and methanol at 170° and higher, tetramethylammonium iodide and phosphoric acid were formed. A mixture of 1 g of 1-amino-1-methylethylphosphonic acid, 3 ml of methyl iodide, and 3 ml of methanol was heated for six hours at 100° in a sealed glass tube. Excess of methyl iodide and methanol was distilled from the dark-colored liquid obtained, and a nondistilling sirupy residue remained. This was dissolved in a little water, treated with an excess of freshly precipitated silver oxide, and filtered. The filtrate was saturated with hydrogen sulfide, silver sulfide was removed, and the aqueous filtrate was evaporated on a water bath. The thick sirupy residue, after being vacuum dried over phosphoric oxide and rubbed out with dry ether, was converted into a powder, which was recrystallized from absolute alcohol. The crystallization, which was extremely slow (about three days at 20°) yielded 0.3 g of very hygroscopic colorless crystals, m.p. 140°.

Found %: N 9.2; 9.1; P 20.2; 20.3

$C_4H_{12}NPO_3$. Calculated %: N 9.2; P 20.3

Diethyl 1-Methyl-1-methylaminoethylphosphonate Hydriodide (II). Methyl iodide (1.42 g) was added to a solution of 1.95 g of diethyl 1-amino-1-methylethylphosphonate in 10 ml of dry ether, and the mixture, contained in a closed flask, was placed in the dark at room temperature. Crystals gradually appeared on the walls of the flask. After six days the solid present was separated from the solution and recrystallized from a mixture of absolute alcohol and ether, when 0.6 g of colorless crystals, m.p. 95°, was obtained. This substance is extremely hygroscopic. It is readily soluble in water, methanol, and ethanol, but insoluble in ether.

Found %: C 28.1; 28.2; H 6.3; 6.4; N 4.9; 4.7; P 10.0; 9.8

$C_8H_{21}PNIO_3$. Calculated %: C 28.5; H 6.2; N 4.2; P 9.2

Diethyl 1-Methyl-1-methylaminoethylphosphonate (III). Methyl iodide (5.7g) was added to a solution of 7.8 g of diethyl 1-amino-1-methylethylphosphonate in 30 ml of ether, and the mixture was set aside for five days. The crystals formed were separated from the liquid and then treated with 5% aqueous NaOH and ether. The ether layer was separated from the aqueous layer, which was extracted with a fresh portion of ether. The combined ether extracts were dried with sodium sulfate. The residue after removal of ether was vacuum-fractionated, and a fraction, amounting to 2.9 g (35%) and boiling at 77-81° (4 mm) was collected. It was slightly yellowish clear mobile liquid having n_D^{18} 1.4370; d_4^{20} 1.0193. Found: MR 53.6. Calculated: MR 53.7.

Found %: N 6.3; 6.3; P 15.0; 15.0

$C_6H_{16}NPO_3$. Calculated %: N 6.7; P 14.8

1-Dimethylamino-1-methylethylphosphonic Acid (IV). A mixture of 3.9 g of 1-amino-1-methylethylphosphonic acid, 4.4 g of 40% formaldehyde solution, and 3.4 g of 77% formic acid was heated in a flask under reflux in a boiling water bath. There was a brisk evolution of carbon dioxide, which gradually slowed down and stopped completely after eight hours. The mixture was then heated at 125° for 40 minutes. The reaction mixture was evaporated down, and the solid residue was recrystallized from 70% alcohol. The product was 3.3 g (79.6%) of colorless crystals, readily soluble in water, but insoluble in ether, benzene, and other organic solvents. Aqueous solutions of the substance are acid to litmus and it can be titrated as a monobasic acid in presence of phenolphthalein as indicator. The substance melts with decomposition at 220-223°.

Found %: C 36.0; 36.1; H 8.4; 8.2; N 8.5; 8.4; P 18.7; 18.6

$C_5H_{14}NPO_3$. Calculated %: C 35.9; H 8.4; N 8.4; P 18.6

Values of 168.9 and 166.6 were found for the equivalent weight, determined by titration with 0.1 N NaOH to phenolphthalein; the calculated equivalent weight is 167.

α-Dimethylaminobenzylphosphonic Acid (V). A mixture of 2.5 g of α-aminobenzylphosphonic acid, 2 g of 40% formaldehyde, and 1.6 g of 77% formic acid was heated in a flask under reflux in a boiling water bath. Evolution of carbon dioxide ceased after 2 hours 30 minutes. The liquid part of the reaction mixture was then distilled off under reduced pressure, and the residual hygroscopic solid was dried in a desiccator and dissolved in 3 ml of absolute alcohol. Alcoholic aniline (2 ml of alcohol and 4 ml of aniline) was added to the solution. The crystals of the aniline salt which had separated by the next day were filtered off and recrystallized twice from 95% ethanol. In the course of this treatment the salt was freed from aniline. The product, amounting to 0.8 g (26%), was a crystalline substance, melting with decomposition at 230°.

Found %: N 6.6; 6.5; P 14.3; 14.4

$C_9H_{14}PNO_3$. Calculated %: N 6.5; P 14.4

An aqueous solution of the substance was titrated with 0.1 N NaOH to phenolphthalein, and a value of 225 was found for the equivalent weight (calculated value 215).

SUMMARY

1. The alkylation of 1-aminoalkylphosphonic acids and their esters was investigated.

2. It was shown that the reaction of 1-aminoalkylphosphonic esters with methyl iodide can be used for the preparation of monomethyl derivatives; dimethyl derivatives can be prepared by the smooth reaction that occurs with formaldehyde and formic acid; and for the preparation of fully methylated 1-aminoalkylphosphonic acids, reaction with dimethyl sulfate in aqueous alkaline solution can be used.

3. The following substances were prepared and characterized: 1-amino-1-methylethylphosphonic acid trimethylbetaines; diethyl 1-methyl-1-methylaminoethylphosphonate hydriodide; 1-dimethylamino-1-methylethylphosphonic acid; and α-dimethylaminobenzylphosphonic acid.

LITERATURE CITED

[1] M.I. Kabachnik and T. Ya. Medved, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, No. 6, 1126. (T.p. 999)*.

[2] T. Ya. Medved and M.I. Kabachnik, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1951, No. 5, 620.

[3] M.I. Kabachnik and T. Ya. Medved, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, No. 5, 868, (T.p. 769)*; T. Ya. Medved and M.I. Kabachnik, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 2, 314, (T.p. 255)*.

---

[*] T.p. = C.B. Translation pagination.

Received January 18, 1955

Institute of Heteroorganic Compounds of the USSR Academy of Sciences

REFORMING OF TUIMAZIN GASOLINE IN CONTACT WITH TROSHKOV KAOLIN

N.I. Shuikin and E.A. Timofeeva

We have studied the catalytic properties of Troshkov kaolin under the conditions applying in the refining of the middle fraction (170-300°) from the primary tar of Budagov sapropelites [1], in the desulfurizing of various gasolines [2], and in the transformations of individual hydrocarbons of various classes [3-5]. It was shown in these investigations that Troshkov kaolin has many valuable catalytic properties: ability to bring about the cracking, isomerization, alkylation, and dehydrocyclization of hydrocarbons, disproportionation of hydrogen, and also desulfurization.

In the present investigation our object was to explore the possibility of effecting a substantial increase in the octane number of Tuimazin gasoline by bringing it into contact with activated Troshkov clay at atmospheric pressure. As the result of experiments on the reforming of the whole gasoline in contact with the clay, and also of the same gasoline after the separation of detonating centers (n-alkanes), we succeeded in finding conditions under which the octane rating of the gasoline was considerably increased – up to 72.0 and 76.8 in presence of 1.5 ml of ethyl fluid (TEL, i.e. tetraethyllead).

EXPERIMENTAL

The experiments on the reforming of gasoline were carried out in the usual flow-type apparatus at 500° at a space velocity of 0.3 hr^{-1}. The contents of sulfonatable compounds were determined by treating the original gasoline and the catalyzates with 2% oleum; their iodine numbers were determined by the Margosches method [6]; sulfur contents by the lamp method [6], and octane numbers by the motor method. The composition of the kaolin is given in one of our previous papers [1]. The clay was activated with sulfuric acid.

The properties of the original Tuimazin gasoline are given in Table 2.

Catalytic Treatment of Tuimazin Gasoline in presence of Activated Troshkov Clay

A head fraction boiling up to 66° (18% by weight) was separated from the original gasoline by fractionation through a 20-plate column. The gasoline, freed from the head fraction, was subjected to reforming in contact with activated Troshkov clay [100 ml (73.0 g) of catalyst, layer 360 mm in length catalysis tube diameter 18 mm] at 500° at a space velocity of 0.3 hr^{-1}. Altogether, 1200 ml (887 g) of gasoline was passed over the catalyst (without its being regenerated). After the catalyst had been regenerated, 300 ml (196 g) of the head fraction of the gasoline was passed over the catalyst at 400° and at the same space velocity. From 100 ml of gasoline 3.27 liters of gas was obtained, and this contained 22.9% of unsaturated hydrocarbons, 12.3% of hydrogen, and 64.8% of alkanes. Table 1 gives the properties of the original head fraction and gasoline freed from head fraction, and also of the catalyzates derived from these.

The catalyzates from the two gasoline fractions were mixed in the appropriate proportions. The properties of the gasoline so obtained are given in Table 2.

Thus, as the result of the catalytic treatment of Tuimazin gasoline in presence of activated Troshkov clay, the sulfur content is reduced by a factor of 18.5 and the fractional composition is improved. The octane number of gasoline with 1.5 ml of TEL is increased by 19.5. The group composition of the gasoline is changed: the content of aromatic hydrocarbons is increased by 11%, the content of cyclohexane hydrocarbons is reduced by one-half, the content of cyclopentane hydrocarbons is increased somewhat, and the content of alkanes is reduced.

Reforming of Tuimazin Gasoline in Contact with Activated Troshkov Clay after Prior Removal of Detonating Centers

The whole gasoline was distilled through a 20-plate column and 6° fractions containing n-alkanes were separated. From 6544.6 g of gasoline we obtained:

1) Fractions containing n-alkanes . . . . 1496.2 g
including:

Hexane fraction	66.0 – 72.0°	288.4 g
Heptane "	95.0 – 101.0°	402.9 g
Octane "	122.5 – 128.5°	341.3 g
Nonane "	148.0 – 154.0°	300.0 g
Decane "	171.0 – 178.0°	173.6 g

2) Gasoline without detonating centers . . . . 4956.4 g
including the head fraction . . . . 690.1 g

3) Losses . . . . 102.0 g

From the fractions containing n-alkanes, aromatic hydrocarbons and sulfur compounds were separated by adsorption on silica gel. These fractions were then fractionated through a 70-plate column. The properties of the n-alkane concentrates then obtained are given in Table 3.

The data in Table 3 show that the properties of the n-alkane concentrates obtained from the gasoline are fairly close to those of the corresponding pure hydrocarbons.

TABLE 1

Properties of Distillates from the Original Gasoline and their Catalyzates

Gasoline	n_D^{20}	d_4^{20}	Sulfur content (%)	Sulfonatable hydrocarbons (% by vol.)
Original gasoline freed from head fraction	1.4193	0.7491	0.141	12.0
Its catalyzate	1.4230	0.7519	0.009	22.5
Head fraction	1.3710	0.6537	0.121	–
Its catalyzate	1.3720	0.6446	0.011	–

The gasoline without the n-alkanes and the head fraction was subjected to reforming in contact with activated Troshkov clay at 500° at a space velocity of 0.3 hr^{-1}. Over 100 ml of catalyst, 944 ml (698.6 g) of gasoline was passed; the catalyst was not regenerated. The head fraction was treated separately at 400° at the same velocity. The catalyzates were mixed to give the gasoline whose properties are presented in Table 2. Thus, as a result of the refining of the gasoline by this method its octane number was increased by 18.7 units in absence of TEL and by 24.3 units in presence of 1.5 ml of TEL. The amount of aromatic hydrocarbons was increased by 13% by volume, the sulfur content suffered a sevenfold reduction, and the content of low-boiling fractions was increased. There can be no doubt that, if required, n-alkanes could be prepared from Tuimazin gasoline in a higher degree of purity.

Effect of Thermal Treatment on the Properties of Tuimazin Gasoline

In order to determine the effect of a purely thermal treatment on the properties of the gasoline, 500 ml of the whole Tuimazin gasoline was passed at 500° and at the same velocity as in the catalytic reforming experiments through the catalysis tube filled with glass wool. The resulting gasoline, obtained in 89.0% yield, had n_D^{20} 1.4144 and d_4^{20} 0.7403, contained 0.09% of sulfur and 13.5% of sulfonatables, and had an iodine number of 8.2 and an octane number of 62.0 in presence of 1.5 ml of TEL. Thus, one thermal treatment on Tuimazin gasoline has a lower refining effect than contact with Troshkov kaolin under the same conditions.

TABLE 2

Yield (% on original gasoline)	n_D^{20}	d_4^{20}	Sulfur content (%)	Iodine number	Sulfonatable hydrocarbons (% by volume)	Octane number without TEL	Octane number with 1.5 ml of TEL	Fractional composition (°C)					Residue and losses (ml)	Group composition (% by weight)			
								Beginning of boiling	10 ml	30 ml	50 ml	98 ml		Aromatic hydrocarbons	Cyclopentane hydrocarbons	Cyclohexane hydrocarbons	Alkanes
Original gasoline																	
–	1.4193	0.7390	0.185	2.2	10.0	37.3	52.5	60	84	107	130	200	2	12.0	13.9	12.7	61.4
Gasoline obtained by refining in presence of activated Troshkov clay																	
87.2	1.4180	0.7430	0.010	0.0	–	–	72.0	58	90	110	127	194	2	23.0	15.3	6.6	55.1
Gasoline obtained by removal of detonating centers and then reforming in contact with activated Troshkov clay																	
84.1*	1.4200	0.7391	0.027	1.2	23.0	56.0	76.8	38	70	92	124	195	2	–	–	–	–

---

* Including 76.0% of gasoline and 7.5% of n-alkanes

TABLE 3

Properties of n-Alkane Concentrates Separated from Tuimazin Gasoline

n-Alkane	B.p. (°C) corrected)	Properties of concentrates		Yield (% by volume on original gasoline)	Properties according to literature [7]		
		n_D^{20}	d_4^{20}		n_D^{20}	d_4^{20}	B.p. (°C, corrected)
Hexane	68.2-69.2	1.3765	0.6609	2.0	1.37506	0.65942	68.8
Heptane	98.0 99.0	1.3890	0.6849	2.8	1.38774	0.68375	98.4
Octane	125.0-126.0	1.4025	0.7103	1.7	1.39764	0.70283	125.6
Nonane	150.3-151.3	1.4091	0.7197	0.6	1.40562	0.71790	150.7
Decane	173.6-174.6	1.4162	0.7312	0.4	1.41206	0.72985	174.0

SUMMARY

1. The conditions were determined for the catalytic refining of Tuimazin gasoline in presence of activated Troshkov kaolin.

2. After direct contact of Tuimazin gasoline with Troshkov kaolin at 500°, the octane number of the gasoline was increased from 37.3 without TEL (52.5 with 1.5 ml of TEL) to 72.0 with 1.5 ml of TEL.

3. Reforming under similar conditions of gasoline from which part of the n-alkanes has been removed yields a gasoline having an octane number of 56.0 without TEL and 76.8 with 1.5 ml of TEL.

LITERATURE CITED

[1] N.I. Shuikin and E.A. Timofeeva, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1951, No. 6, 728.

[2] E.A. Timofeeva, N.I. Shuikin, and V.M. Kleimenova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, No. 3,789 (T.p. 713)*

[3] N.I. Shuikin and E.A. Timofeeva, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, No. 4, 678 (T.p. 607)*

[4] E.A. Timofeeva and N.I. Shuikin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No. 6, 1075 (T.p. 937)*

[5] N.I. Shuikin and E.A. Timofeeva, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 2, 314 (T.p. 281)*

[6] Test Methods for Petroleum Products, State Fuel Tech. Press Moscow and Leningrad, 1949.

[7] Gustav Egloff, Physical Constants of Hydrocarbons, I. Reinhold Publishing Corporation, N.Y. 1939, pp 36, 40, 48, 60, 67.

Received December 8, 1954

N.D. Zelinsky Institute of Organic Chemistry of the USSR Academy of Sciences

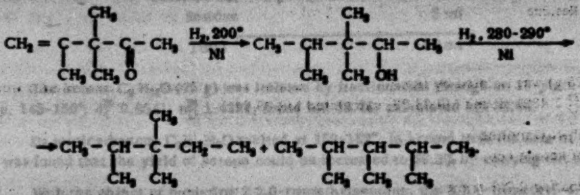
---

* T.p. = C.B. Translation pagination.

REACTIONS OF 3,3,4-TRIMETHYL-2-PENTANOL

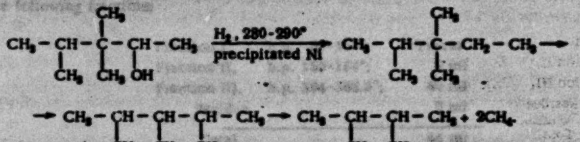
A.P. Meshcheryakov and L.V. Petrova

With the object of preparing 2,3,3-trimethylpentane from 3,3,4-trimethyl-2-pentanol, we studied the reactions of this alcohol under the conditions of hydrogenational catalysis, and also of its acetic ester under pyrolysis conditions. In hydrogenational catalysis at 100-120 atm and 280-290°, dehydration of the alcohol is accompanied by isomerization, and the main product is 2,3,4-trimethylpentane with only a small amount of 2,3,3-trimethylpentane:



$$CH_2=C(CH_3)-C(CH_3)_2-C(=O)-CH_3 \xrightarrow[Ni]{H_2,\,200°} CH_3-CH(CH_3)-C(CH_3)_2-CH(OH)-CH_3 \xrightarrow[Ni]{H_2,\,280-290°} CH_3-CH(CH_3)-C(CH_3)_2-CH_2-CH_3 + CH_3-CH(CH_3)-CH(CH_3)-CH(CH_3)-CH_3$$

When hydrogenation is carried out over a nickel catalyst precipitated on silica gel at 100-120 atm and 280-290°, demethylation occurs:



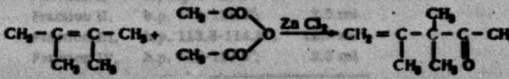
$$CH_3-CH(CH_3)-C(CH_3)_2-CH(OH)-CH_3 \xrightarrow[\text{precipitated Ni}]{H_2,\,280-290°} CH_3-CH(CH_3)-C(CH_3)_2-CH_2-CH_3 \rightarrow CH_3-CH(CH_3)-CH(CH_3)-CH(CH_3)-CH_3 \rightarrow CH_3-CH(CH_3)-CH(CH_3)-CH_3 + 2CH_4$$

Our experiments on the dehydration of 3,3,4-trimethyl-2-pentanol with acetic anhydride in presence of anhydrous sodium acetate by the method of Hickinbottom and Porter [1] showed that the dehydration of this secondary alcohol does not go, even after long boiling (48 hours).

According to various investigations [2-6], pyrolysis of the acetic ester of 3,3,4-trimethyl-2-pentanol should yield only 3,3,4-trimethyl-1-pentene, but it was found that, in the pyrolysis of the acetic ester of this highly ramified alcohol, isomerization again occurred, and a mixture of two isomers was obtained: 2,3,4-trimethyl-1-pentene and 3,3,4-trimethyl-1-pentene. Only by the Grignard synthesis did we succeed in preparing 2,3,3-trimethylpentane in the pure state.

EXPERIMENTAL

3,3,4-Trimethyl-2-pentanol was prepared by the hydrogenation of 3,3,4-trimethyl-4-penten-2-one, which was synthesized from 2,3-dimethyl-2-butene and acetic anhydride in presence of zinc chloride:



$$CH_3-C(CH_3)=C(CH_3)-CH_3 + (CH_3-CO)_2O \xrightarrow{ZnCl_2} CH_2=C(CH_3)-C(CH_3)_2-C(=O)-CH_3$$

2,3-Dimethyl-2-butene was prepared by the dehydration of pinacol at 200-220° over a catalyst (20% of zinc chloride on a pumice carrier) at a space velocity of 0.2 hr^{-1}. The crude olefin was separated from water, dried over calcium chloride, and fractionated through an 18-plate column. The yield was 60%. The constants of the 2,3-dimethyl-2-butene were b.p. 70-73°; d_4^{20} 0.7007; n_D^{20} 1.4060; found MR 29.44; calculated MR 29.35.

The ketone was synthesized by Kondakov's method [7] under the conditions described in Meshcheryakov and Petrova's paper. 2,3-Dimethyl-2-butene (35 g) and acetic anhydride (42.5 g) were introduced simultaneously into a 250-ml round-bottomed flask having two side openings. The reaction was carried out at 10-20° for eight hours with constant stirring. The reaction flask was then cooled with ice, and the reaction product was decomposed with cold water. The upper layer was separated, washed (with water, with saturated sodium carbonate solution, and again with water), dried over calcium chloride, and fractionated from a Favorsky flask. The product had a strong camphor odor. The amount of the product taken for fractionation was 40 ml, and the following fractions were obtained:

Fraction I,	b.p. 63-140°;	9 ml
Fraction II,	b.p. 142-153°;	30 ml
Fraction III,	b.p. 153-165°;	4 ml
Residue		5 ml
Total		48 ml

The ketone $C_8H_{14}O$ (25 g) was isolated by fractionation through an 18-plate column. Its constants were b.p. 145-150°; d_4^{20} 0.8541; n_D^{20} 1.4321; found MR 38.25; calculated MR 38.64.

Its semicarbazone $C_9H_{17}N_3O$ melted at 150-152°, in accord with the data of Colonge and Mostafavi [8]. It was found that the yield of ketone could be increased to 69.3% by carrying out the synthesis at 0°.

With the object of preparing 2,2,3-trimethylpentane, the 3,3,4-trimethyl-4-penten-2-one that we had prepared was hydrogenated at 200° at 100-120 atm in an autoclave over a mixed catalyst (15 g of alumina and 30 g of A.A. Bag's nickel catalyst). For the hydrogenation, 50 g of the ketone and 15% of nickel catalyst + 15% of alumina were taken, and 45 ml of hydrogenation product was obtained, the fractionation of which gave the following fractions:

Fraction I,	b.p. 50-150°;	Traces
Fraction II,	b.p. 150-164°;	2 ml
Fraction III,	b.p. 164-166.5°;	40 ml
Residue		2 ml
Total		44 ml

The main hydrogenation product b.p. 164-166.5°, was found to be 3,3,4-trimethyl-2-pentanol, d_4^{20} 0.8557; n_D^{20} 1.4381; found MR 39.38; calculated MR 39.56. The hydroxyl content was determined by the Chugaev-Tserevitinov method.

Found %: OH 12.0
$C_8H_{18}O$. Calculated %: OH 13.1

At 200°, therefore, hydrogenation of the unsaturated ketone goes only as far as the alcohol.

In order to obtain 2,3,3-trimethylpentane, the 3,3,4-trimethyl-2-pentanol was hydrogenated over the same catalyst, but at 280-290°. The hydrogenation product was extracted from the autoclave with ethanol, which was then removed by repeated washing with water. The hydrocarbon was separated, dried over calcium chloride, and fractionated over sodium through an 18-plate column, 20 ml being taken for the fractionation:

Fraction I,	b.p. up to 112°;	3.5 ml
Fraction II,	b.p. 112-113.8°;	2.0 ml
Fraction III,	b.p. 113.8-114.8°;	12.0 ml
Fraction IV,	b.p. 115-120.0°;	2.3 ml
	Total	19.8 ml

Refractionation of the 113.8-114.8° and 112-113.8° fractions over sodium gave the fractions:

Fraction I,	b.p. up to 113.6°;	2.2 ml
Fraction II,	b.p. 113.8-114.8°;	10.0 ml
Fraction III,	b.p. 115-120°;	0.8 ml
	Total	13.0 ml

The hydrocarbon had b.p. 113.8-114.8°; d_4^{20} 0.7218; n_D^{20} 1.4060; found MR 38.86; calculated MR 39.14.

The structure of the hydrocarbon obtained was established by Raman spectrum analysis. It was found that isomerization had occurred during the hydrogenation process, and instead of only the expected 2,3,3-trimethylpentane, 2,3,4-trimethylpentane was formed in predominating amount together with some 2,3,3-trimethylpentane.

When 3,3,4-trimethyl-2-pentanol was hydrogenated at 100-120 atm and 280-290° over a nickel catalyst precipitated on silica gel, the main fraction of the resulting catalyzate had b.p. 56-58°; n_D^{20} 1.3950; d_4^{20} 0.6750; found MR 29.07; calculated MR 29.90.

The Raman spectrum showed that the 56-58° fraction consisted almost entirely of 2,3-dimethylbutane. Under these conditions, therefore, the hydrogenation product 2,3,3-trimethylpentane is demethylated to 2,3-dimethylbutane.

With the object of preparing 2,3,3-trimethylpentane by the hydrogenation of 3,3,4-trimethyl-1-pentene, we carried out experiments on the preparation of 3,3,4-trimethyl-1-pentene by the thermal degradation of the acetic ester of 3,3,4-trimethyl-2-pentanol by Hickinbottom's method. The acetic ester was prepared by Spassow's method [9]:

$$2C_8H_{17}OH + 2CH_3COCl + Mg = MgCl_2 + H_2 + 2C_{10}H_{20}O_2$$

A mixture of 6 g of magnesium, 25 g of 3,3,4-trimethyl-2-pentanol (dried with potassium carbonate and twice distilled over sodium), and 50 g of absolute ether was prepared in a 500-ml round-bottomed flask. The mixture was shaken while a solution of 27.3 g of acetyl chloride in 50 ml of absolute ether was added from a dropping funnel. When the whole of the acetyl chloride had been added, the reaction mixture was set aside in a bath of cold water for one hour and was then heated at 40-50° for two hours. The solid reaction product was cooled with ice water and decomposed with a cooled potassium carbonate solution (20 g of potassium carbonate in 250 ml of water). The mixture was extracted with three successive 35-ml portions of ether, and the ether extracts were dried over calcium chloride. The ether was distilled off through an 18-plate column, and the acetic ester was dried over sodium sulfate. The yield of acetic ester was 58.6%.

The acetic ester $C_{10}H_{20}O_2$ was vacuum-fractionated twice. The following fractions were obtained at 12-13 mm:

Fraction I,	b.p. 56-63°;	4.5 g
Fraction II,	b.p. 65-67°;	20.0 g (acetic ester):

d_4^{20} 0.8821; n_D^{20} 1.4259; found MR 49.95; calculated MR 50.03

The pyrolysis of the acetic ester of 3,3,4-trimethyl-2-pentanol was carried out in a 20 mm quartz tube filled with glass wool (50 g). The tube was placed in an electric furnace, and the pyrolysis was carried out at 430-450°, the acetic ester being supplied at the rate of 25 ml per hour. The pyrolyzate was collected in a receiver cooled with ice water; it was washed with water and 10-15% sodium carbonate solution to free it from acetic acid, and was dried over calcium chloride.

It was found that the pyrolysis of the acetic ester of 3,3,4-trimethyl-2-pentanol does not go at 250-350°; it goes only to a slight extent at 410-420°; and complete breakdown of the acetic ester into olefin and acetic acid occurs only at 430-460°.

Three fractionations of 7.5 g of the product yielded:

Fraction I.	b.p. 95-103°;	0.2 g
Fraction II.	b.p. 103-106°;	4.2 g (olefin)
Fraction III.	b.p. 110-120°;	1.5 g
Fraction IV.	b.p. 120-160°;	1.2 g
	Total	7.1 g

The main fraction was found to have b.p. 103.0-106.0°; d_4^{20} 0.7310; n_D^{20} 1.4158; found MR 38.38; calculated MR 38.67. The boiling point of 3,3,4-trimethyl-1-pentene is 105° [10], and that of 2,3,4-trimethyl-1-pentene is 106.7-107.7° [11].

In order to prove the structure of the olefin obtained, it was oxidised with 2% aqueous potassium permanganate. It was shown that the acid $C_7H_{14}O_2$ was present among the oxidation products. Titration with 0.1 N NaOH gave:

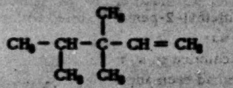
Found K 305;
Calculated K 308,

K being the acid equivalent. The amide was prepared, $C_{17}H_{15}ONH_2$, m.p. 130-132°. The literature gives m.p. 133-134° for the amide $C_{17}H_{15}ONH_2$.

The ketone $C_7H_{14}O$ was isolated from the oxidation products; it had b.p. 128-130°; d_4^{20} 0.8054; n_D^{20} 1.4005; found MR 34.22; calculated MR 34.53. It gave a 2,4-dinitrophenylhydrazone, m.p. 93°.

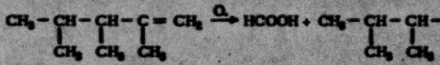
Found %: N 19.02
$C_{13}H_{18}N_4O_4$. Calculated %: N 19.07

According to Hickinbottom, in the hydrolysis of the acetic ester, only 3,3,4-trimethyl-1-pentene



$$CH_3-\underset{CH_3}{CH}-\overset{CH_3}{\underset{CH_3}{C}}-CH=CH_2$$

should be formed, and oxidation of this will give 2,2,3-trimethylbutyric and formic acids. However, oxidation with 2% aqueous potassium permanganate gave not only 2,2,3-trimethylbutyric acid, but also a ketone, b.p. 128-130°. The formation of the ketone $C_7H_{14}O$ indicates that in the pyrolysis of the acetic ester of 3,3,4-trimethyl-2-pentanol the resulting 3,3,4-trimethyl-1-pentene undergoes isomerization with formation of 2,3,4-trimethyl-1-pentene. Oxidation of the latter with 2% aqueous potassium permanganate gives formic acid and 3,4-dimethyl-2-pentanone:



$$CH_3-\underset{CH_3}{CH}-\underset{CH_3}{CH}-\underset{CH_3}{C}=CH_2 \xrightarrow{O_2} HCOOH + CH_3-\underset{CH_3}{CH}-\underset{CH_3}{CH}-COCH_3$$

In order to establish the structure of the ketone obtained, 3,4-dimethyl-3-penten-2-one was synthesized from 2-methyl-2-butene by Kondakov's method [12], and this was then hydrogenated at room temperature over platinized charcoal (5% Pt). The boiling point of 3,4-dimethyl-2-pentanone was 133-135°, and it had d_4^{20} 0.8273; n_D^{20} 1.4087; found MR 34.10; calculated MR 34.53.

The 2,4-dinitrophenylhydrazone was prepared; it melted at 94-95°. A mixture of the 2,4-dinitrohydrazone of the ketone $C_7H_{14}O$ which we prepared by the oxidation of the olefin C_8H_{16} and the 2,4-dinitrophenylhydrazone of the ketone obtained in the confirmatory synthesis melted at 93-94°; i.e. there was no depression.

For comparison with the hydrocarbons obtained in the course of the transformations of 3,3,4-trimethyl-2-pentanol under the conditions of hydrogenational catalysis and also under the conditions of the pyrolysis of its acetic ester, 2,3,3-trimethylpentane was prepared by Grignard synthesis from 2-chloro-2,3-dimethylbutane and ethylmagnesium bromide. 2-Chloro-2,3-dimethylbutane was prepared by shaking a mixture of 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene with twice its volume of hydrochloric acid (sp. gr. 1.19) at room temperature for two hours. It had b.p. 108-110°; n_D^{20} 1.4168; d_4^{20} 0.8781; found MR 34.33; calculated MR 34.77.

The materials taken for the synthesis were 2-chloro-2,3-dimethylbutane (180 g), magnesium (36 g of turnings), ethyl chloride (96 g), and absolute ether (800 ml).

After decomposition of the reaction product and treatment by the usual methods, two fractionations yielded 2,3,3-trimethylpentane, b.p. 114-114.5°, in 29% yield. Traces of unsaturated hydrocarbons were removed from the 114-114.5° fraction by Tsvet's chromatographic adsorption method [14], which has been applied to the separation of hydrocarbons by Kazansky and Mikhailova, and the hydrocarbon was then again distilled over sodium. The following fractions were obtained:

Fraction I,	b.p. 102-114°;	1 ml
Fraction II,	b.p. 114-114.5°;	53 ml
Residue		5 ml
	Total	59 ml

The constants of the hydrocarbon were d_4^{20} 0.7275; n_D^{20} 1.4073; found MR 38.48; calculated MR 39.14.

Raman spectrum analysis showed that this hydrocarbon consisted only of 2,2,3-trimethylpentane.

SUMMARY

1. It was shown that, under the conditions of catalytic hydrogenation at 280-290° and 100-120 atm, 3,3,4-trimethyl-2-pentanol yields a mixture of 2,3,3- and 2,3,4-trimethylpentanes, the latter predominating. The formation of this mixture of isomers is due to the isomerization of the initial reaction product, 3,3,4-trimethyl-1-pentene.

2. It was shown that in the pyrolysis of the acetic ester of 3,3,4-trimethyl-2-pentanol at 430-450° isomerization again occurs, not only 3,3,4-trimethyl-1-pentene being formed, but also much 2,3,4-trimethyl-1-pentene [4]. This method for the preparation of hydrocarbons cannot therefore be recommended as a general method for the preparation of the higher branched olefins.

3. For comparison with the octane isomers obtained by the hydrogenation of 3,3,4-trimethyl-2-pentanol and by the pyrolysis of its acetic ester, 2,3,3-trimethylpentane was synthesized by the Grignard method.

LITERATURE CITED

[1] W.I. Hickinbottom, G. Porter, J. Inst. Petr., 35, 621 (1949).

[2] P. Cramer, M. Mulligan, J. Am. Chem. Soc., 58, 373 (1939).

[3] F. Whitmore, H. Rotrock, J. Am. Chem. Soc., 55, 1106 (1933).

[4] A. Pelt, Y. Wibaut, Rec. trav. chim., 57, 1055 (1938).

[5] A. Pelt, Y. Wibaut, Rec. trav. chim., 55, 1941 (1941).

[6] R. Ya. Levina, A.A. Faiezilberg, T.I. Tantsyreva, and E.G. Treshchova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1951, No. 3, 321.

[7] I.L. Kondakov, J. Russ. Chem. Soc. 26, 232 (1894).

[8] I. Colonge and K. Mostafavi, Bull. Soc. chim. 6, 353 (1939).

[9] A. Spassow, Organic Syntheses, Collected Vol. 3, 124 (1952).*

[10] Selected Values of Properties of Hydrocarbons, Washington (1947).

[11] G. Egloff. Physical Constants Hydrocarbons V. II, 1939 (1940).

[12] I.L. Kondakov, J. Russ. Chem. Soc., 26, 229, (1894).

[13] A. Haller, E. Bauer, Comptes Rend. 148, 6 (1909).

---

* p. 390 in original American edition. — Publisher.

[14] M.S. Tsvet, Chromatographic Adsorption Analysis, Acad. Sci. USSR Press, 1946.

[15] A.P. Meshcheryakov and E.P. Kaplan, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1938, 1066.

Received January 19, 1955

N.D. Zelinsky Institute of Organic Chemistry of the USSR Academy of Sciences.

REACTIONS OF SYMMETRICAL AROMATIC MERCURY COMPOUNDS WITH PHENOLS

M.M. Koton and V.F. Martynova

Dimroth [1] was the first to show that the halides and acetate of mercury are able to mercurate aromatic hydrocarbons and their derivatives with formation of mono-, di-, and tri-mercurated compounds. The mercuration of phenols and amines proceeds particularly readily.

Koton and coworkers [2] showed that dialkyl and diaryl mercury compounds very readily mercurate phenols with formation of new organomercury compounds:

$$R_2Hg + R'\,C_6H_4OH \rightarrow RH + RHg\,C_6H_3\,(OH)\,R'.$$

In the present investigation we have continued the study of this reaction: we have examined the behavior of diphenylmercury derivatives of general formula $(RC_6H_4)_2$ Hg with the object of determining the effect of the nature of the substituent R in the benzene ring of the organomercury compound on the rate and character of the reactions occurring with various phenols. For this purpose we took the following compounds:

1. Bis-p-aminophenylmercury $(p\text{-}H_2NC_6H_4)_2Hg$
2. Bis-o-hydroxyphenylmercury $(o\text{-}HOC_6H_4)_2Hg$
3. Bis-p-methoxyphenylmercury $(p\text{-}CH_3OC_6H_4)_2Hg$
4. Bis-m-nitrophenylmercury $(m\text{-}O_2NC_6H_4)_2Hg$
5. Bis-o-nitrophenylmercury $(o\text{-}O_2NC_6H_4)_2Hg$
6. Bis-p-carboxyphenylmercury $(p\text{-}HOOCC_6H_4)_2Hg$

The following phenols were used: pyrogallol, hydroquinone, resorcinol, phenol, p-cresol, p-aminophenol, p-nitrophenol, o-nitrophenol, m-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol, p-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol.

Mercuration with symmetrical mercury compounds of formula $(RC_6H_4)_2Hg$ requires the application of heat. On the basis of a radical mechanism for this reaction, it might be expected that the readiness with which mercuration occurs would depend on the thermal stability of the symmetrical mercury compound, low stability being associated with ready reaction with phenols.

A study was made of the thermal stability of symmetrical organomercury compounds at 130-150°. The experiments showed that the thermal stabilities of compounds of formula $(RC_6H_4)_2Hg$ vary greatly. Organomercury compounds in which the substituent R in the benzene ring is COOH or NO_2, i.e. substituents of the "second kind", are thermally stable. Organomercury compounds in which R is NH_2, OH or OCH_3, i.e. substituents of the "first kind", decompose already at 130° with separation of mercury, the amount of mercury separating being dependent on the nature of the substituent in the benzene ring.

With respect to the extent of decomposition in three hours at 130°, these compounds can be arranged in the following series:

$$(p\text{-}H_2NC_6H_4)_2\,Hg > (o\text{-}HOC_6H_4)_2\,Hg > (p\text{-}CH_3OC_6H_4)_2\,Hg$$

However, in our study of thermal decomposition we were unable to determine the difference in stability between compounds of formula $(RC_6H_4)_2Hg$ having substituents of the "second kind" (i.e. NO_2 or COOH), because of their very high thermal stability (as shown in Table 1).

One of the present authors has shown [3] that polyhydric phenols (pyrogallol and others) accelerate the thermal decomposition of symmetrical mercury compounds, and we therefore studied the decomposition of $(RC_6H_4)_2Hg$ in presence of pyrogallol at 130° and 150°. Under these conditions symmetrical mercury compounds having substituents of the "second kind" decomposed with separation of mercury (Table 2).

With respect to rate of decomposition these compounds form the series:

$$(m\text{-}NO_2C_6H_4)_2Hg > (o\text{-}NO_2C_6H_4)_2Hg > (p\text{-}HOOCC_6H_4)_2Hg.$$

TABLE 1

Formula of compound	t°C	Time (hours)	Amount of mercury formed (%)	Analysis of residue for mercury	
				Found (%)	Calculated (%)
$(p\text{-}H_2NC_6H_4)_2Hg$	130	3	23.85	52.09	51.94
$(o\text{-}HOC_6H_4)_2Hg$	130	3	20.69	51.77	51.53
$(p\text{-}CH_3OC_6H_4)_2Hg$	130	3	5.05	47.90	48.30
$(m\text{-}NO_2C_6H_4)_2Hg$	150	3	None	45.20	45.04
$(o\text{-}NO_2C_6H_4)_2Ng$	150	3	None	44.97	45.04
$(p\text{-}HOOCC_6H_4)_2Hg$	160	3	None	44.98	44.82

TABLE 2

Formula of compound	t°C	Time (hours)	Amount of mercury formed (%)
$(p\text{-}H_2NC_6H_4)_2Hg$	130	3	86.85
$(p\text{-}CH_3OC_6H_4)_2Hg$	130	3	76.43
$(m\text{-}NO_2C_6H_4)_2Hg$	150	3	58.70
$(o\text{-}NO_2C_6H_4)_2Hg$	150	3	30.70
$(p\text{-}HOOCC_6H_4\ Hg$	150	3	19.28

In order to determine the laws governing the strengths of bonds formed by radicals with mercury atoms in the symmetrical organomercury compounds studied, we investigated their decomposition in presence of monohydric phenols. It was found that, for the compounds containing substituents of the "first kind", the order of ease of decomposition was the same as for thermal decomposition (Table 3).

With respect to thermal stability, therefore, all of the compounds of general formula $(RC_6H_4)_2Hg$ that we have studied can be placed in the following order:

$$(p\text{-}H_2NC_6H_4)_2Hg < (o\text{-}HOC_6H_4)_2Hg < (p\text{-}CH_3OC_6H_4)_2Hg <$$
$$< (m\text{-}NO_2C_6H_4)_2Hg < (o\text{-}NO_2C_6H_4)_2Hg < (p\text{-}HOOCC_6H_4)_2Hg.$$

It was shown further that, in presence of the phenols pyrogallol, p-aminophenol, and hydroquinone, the organomercury compounds studied decompose with separation of mercury and without formation of mercurated compounds. This behavior could be explained in two ways: 1) by the high reducing power of these phenols; or 2) by the extremely low thermal stability of the mercurated derivatives of these phenols. It might be expected, therefore, that phenols of lower reducing power would be able to give stable mercurated derivatives with the symmetrical mercury compounds that we have chosen for investigation. It is in fact found that, when substituted phenols are heated with compounds of formula $(RC_6H_4)_2Hg$, they react with formation of new organomercury compounds.

The results obtained enable us to compare the thermal stabilities of the symmetrical mercury compounds with their reactivities in the mercuration reaction. The least thermally stable of these mercury compounds will mercurate phenols at the lowest temperatures (70-100°) with formation of mono-, di-, and tri-mercurated phenols. For example, when bis-p-aminophenylmercury is used, mono-, di-, and tri-mercurated phenols are formed already at 70° [4].

As the thermal stability of the compound $(RC_6H_4)_2Hg$ increases, its ability to give polymercurated compounds diminishes and more severe reaction conditions are required. For example, the reaction of bis-p-methoxyphenylmercury with phenols was carried out at 130-150°, and the main products were monomercurated derivatives of these phenols of general formula $p\text{-}CH_3OC_6H_4HgC_6H_3(OH)(R)$ [5]. When bis-o or bis-m-nitrophenylmercury was used, the reaction often did not go.

On the basis of our results it must be supposed that the mercuration of phenols by symmetrical mercury compounds passes through a stage in which the mercury compounds decompose into free radicals according to the equation:

$$RC_6H_4 - Hg - C_6H_4R \rightarrow RC_6H_4^{\cdot} + RC_6H_4Hg^{\cdot}.$$

The radical $RC_6H_4^{\cdot}$, then reacts with a hydrogen of the benzene ring of the phenol with formation of the corresponding benzene derivative (aniline, anisole, or nitrobenzene). With respect to reactivity, the radicals formed can be arranged in the following order:

$$(p\text{-}H_2NC_6H_4)^{\cdot} > (o\text{-}HOC_6H_4)^{\cdot} > (p\text{-}CH_3OC_6H_4)^{\cdot} >$$

$$> (m\text{-}NO_2C_6H_4)^{\cdot} > (o\text{-}NO_2C_6H_4)^{\cdot} > (p\text{-}HOOCC_6H_4)^{\cdot}.$$

The sequence that we have found is fully in accord with those found previously by Kharasch, Nesmeyanov, Kocheshnikov, and Koton. It must be pointed out that we were the first to establish the position of the radical of o-nitrophenol in the Nesmeyanov-Kharasch series, and also to determine the relative positions of the o- and m-nitrophenyl radicals. The study of the reactions between symmetrical organomercury compounds and phenols has enabled us to determine some of the laws governing the behavior of substituted phenols. As shown previously, reaction of symmetrical organomercury compounds with phenols results in the formation, on the one hand, of mercurated phenols, and on the other, of metallic mercury. We estimated the reactivities of the phenols on the basis of the amount of mercury that separated in the course of the mercuration reaction; the results were compared with those for unsubstituted phenol.

TABLE 3

Formula of compound	t°C	Amount of mercury formed (%) in reaction with	
		p-aminophenol	hydroquinone
$(p\text{-}H_2NC_6H_4)_2Hg$	130	74.50	72.38
$(p\text{-}CH_3OC_6H_4)_2Hg$	130	58.26	52.20
$(m\text{-}NO_2C_6H_4)_2Hg$	150	19.75	9.50
$(o\text{-}NO_2C_6H_4)_2Hg$	150	8.79	8.21

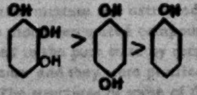
The phenols that we studied can be divided into two groups. The first of these consists of phenols that do not form stable mercurated derivatives; when they are treated with compounds of the type $(RC_6H_4)_2Hg$, only the separation of metallic mercury is observed. The phenols of this group include pyrogallol, p-aminophenol, and hydroquinone. The second group consists of phenols which, when treated with compounds of the type $(RC_6H_4)_2Hg$, give the corresponding mercurated compounds, as well as a little metallic mercury. This group includes phenol, p-cresol, resorcinol, p-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, p-, o-, and m-nitrophenols, 2,4-dinitrophenol, and 2,4,6-trinitrophenol. In their turn, phenols of the second group can be divided into two groups according to the nature of the substituents: 1) phenols having substituents of the "first kind", and 2) phenols having substituents of the "second kind".

When they react with organomercury compounds of the type $(RC_6H_4)_2Hg$, phenols having substituents of the "first kind" yield more metallic mercury than phenols having substituents of the "second kind", with the exception of 2,4,6-trichlorophenol, which behaves like the nitrophenols (Table 4).

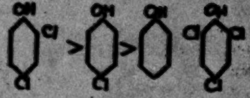
The results of our investigations of the reaction of phenols with symmetrical organomercury compounds of the type $(RC_6H_4)_2Hg$ permit us to make the following general statements:

1) Increase in the number of hydroxyl groups in the benzene ring of phenols results in increase in reactivity.

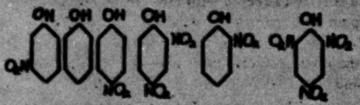
These phenols form the series:



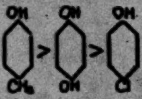
2) Introduction of chlorine atoms into the benzene ring of phenol increases the reactivity, an exception being 2,4,6-trichlorophenol, which is less reactive probably owing to a steric-hindrance effect. The behavior of chlorophenols in reactions with $(RC_6H_4)_2Hg$ can be represented by the following series:



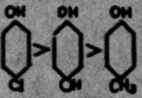
3) Introduction of a nitro group into the benzene ring of phenol lowers the reactivity (with the exception of m-nitrophenol, which is highly reactive). With respect to the extent to which mercury separates in their reactions with organomercury compounds of the type $(RC_6H_4)_2Hg$, nitrophenols may be arranged in the series:



4) It must be noted that the amount of mercury that separates in the reaction of $(RC_6H_4)_2Hg$ with phenols depends both on the nature of the phenol and on the nature of the organomercury compound. Thus, the phenols p-cresol, p-chlorophenol, and hydroquinone in their reactions with bis-p-aminophenylmercury and bis-p-methoxyphenylmercury may be placed in the following order with respect to the amount of mercury that separates:



When the reaction is carried out with bis-m- or bis-o-nitrophenylmercury, the sequence of the phenols is reversed:



The results obtained indicate that the separation of mercury during the mercuration of phenols proceeds through the stage of the formation of mercurated phenols, which are then decomposed; i.e. it is not an independent reaction occurring at the same time as mercuration. The stability of the mercurated phenol will depend not only on the structure of the phenol residue, but also on the nature of the organic radical attached to the mercury atom of the mercurated phenol.

EXPERIMENTAL

In all experiments a mixture of the substances was heated in sealed tubes in thermostats regulated at 50°, 70°, 100°, 130°, and 150° for periods ranging from 1 to 12 hours; 0.5-0.6 g of reactants was taken. When the tubes were opened, it was always found that the corresponding benzene derivative (aniline, anisole, nitrobenzene) was floating on the reaction mixture. This substance was removed and with the object of isolating the solid reaction products, the reaction mixture was extracted successively with various solvents (ether, alcohol, benzene, chloroform). The monomercurated compounds were generally readily soluble in one of these solvents and they were obtained in the pure state by recrystallization. Di- and tri-mercurated compounds are insoluble in organic solvents and they were purified by dissolution in 0.5 N caustic alkali and reprecipitation with carbon dioxide. The structures of some of the mercurated phenols were proved by cleavage with bromine or iodine, when the organomercury radical was replaced by a halogen atom. The resulting bromo- or iodo-phenol was identified by its melting point and by a mixture melting point test.

Mercury was determined volumetrically in the mercurated products. The 44 new mono-, di-, and tri-mercurated phenols listed in Table 5 were prepared and characterized.

TABLE 4

$(RC_6H_4)_2Hg$	Phenol	t°C	Time (hours)	Amount of metallic mercury (%)
$(p\text{-}H_2NC_6H_4)_2Hg$	Pyrogallol	130	3	86.88
$(p\text{-}H_2NC_6H_4)_2Hg$	Hydroquinone	130	3	72.38
$(p\text{-}H_2NC_6H_4)_2Hg$	Phenol	130	3	40.50
$(p\text{-}CH_3OC_6H_4)_2Hg$	Pyrogallol	130	3	76.43
$(p\text{-}CH_3OC_6H_4)_2Hg$	Hydroquinone	130	3	52.20
$(p\text{-}CH_3OC_6H_4)_2Hg$	Phenol	130	3	5.63
$(p\text{-}H_2NC_6H_4)_2Hg$	o-Chlorophenol	150	3	83.71
$(p\text{-}H_2NC_6H_4)_2Hg$	p-Chlorophenol	150	3	80.49
$(p\text{-}H_2NC_6H_4)_2Hg$	Phenol	150	3	68.25
$(p\text{-}H_2NC_6H_4)_2Hg$	Trichlorophenol	150	3	58.00
$(p\text{-}H_2NC_6H_4)_2Hg$	m-Nitrophenol	150	3	80.87
$(p\text{-}H_2NC_6H_4)_2Hg$	p-Nitrophenol	150	3	60.04
$(p\text{-}H_2NC_6H_4)_2Hg$	2,4-Dinitrophenol	150	3	53.79
$(p\text{-}H_2NC_6H_4)_2Hg$	o-Nitrophenol	150	3	10.02
$(p\text{-}H_2NC_6H_4)_2Hg$	Trinitrophenol	150	3	6.00
$(m\text{-}O_2NC_6H_4)_2Hg$	Pyrogallol	150	3	68.70
$(m\text{-}O_2NC_6H_4)_2Hg$	Hydroquinone	150	3	9.60
$(m\text{-}O_2NC_6H_4)_2Hg$	Phenol	150	3	3.56
$(o\text{-}O_2NC_6H_4)_2Hg$	Pyrogallol	150	3	30.70
$(o\text{-}O_2NC_6H_4)_2Hg$	Hydroquinone	150	3	8.70
$(o\text{-}O_2NC_6H_4)_2Hg$	Phenol	150	3	0.00

TABLE 5

No.	Formula of compound	M.p. (°C)	Appearance of crystals	Solubility in organic solvents
1	2	3	4	5
1	$(p\text{-}H_2NC_6H_4Hg)_2C_6H_2(OH)(NO_2)$	Does not melt below 280°	Dark blue	Insoluble
2	$(p\text{-}H_2NC_6H_4Hg)_2C_6H_2(OH)(NO_2)$	Does not melt below 260°	Orange	Ditto
3	$(p\text{-}H_2NC_6H_4Hg)C_6H_2(OH)(NO_2)_2$	203-205	*	In benzene
4	$(p\text{-}H_2NC_6H_4Hg)C_6H(OH)(NO_2)_3$	192-195	*	In chloroform
5	$(p\text{-}H_2NC_6H_4Hg)C_6H_3(OH)(Cl)$	180-181	Yellow	In alcohol
6	$(p\text{-}H_2NC_6H_4Hg)_2C_6H(OH)(Cl)$	Does not melt below 260°	Dark green	Insoluble
7	$(p\text{-}H_2NC_6H_4Hg)_2C_6H(OH)(Cl)_2$	Does not melt below 260°	Dark red	Ditto
8	$(p\text{-}H_2NC_6H_4Hg)_2C_6H(OH)(Cl)_2$	195-197	Green	In alcohol and ether
9	$(p\text{-}H_2NC_6H_4Hg)_2C_6(OH)(Cl)_3$	Does not melt below 260°	Dark blue	Insoluble
10	$(p\text{-}H_2NC_6H_4Hg)_2C_6H_2(OH)_2$	Decomposes at 200°	Light green	Sparingly soluble in alcohol
11	$(p\text{-}H_2NC_6H_4Hg)_2C_6H(NO_2)_2$	Does not melt below 260°	Dark green	Insoluble
12	$(p\text{-}H_2NC_6H_4Hg)_2C_6H_3(OH)$	179	White	In alcohol and chloroform
13	$(p\text{-}H_2NC_6H_4Hg)_2C_6H(OH)CH_3$	Does not melt below 280°	Fine white	Insoluble
14	$(p\text{-}CH_3OC_6H_4Hg)_2C_6H_2(OH)(NO_2)$	Ditto	Yellow	Ditto

TABLE 5 (continued)

1	2	3	4	5
15	$(p\text{-}CH_3OC_6H_4Hg)C_6H_3(OH)(NO_2)$	109-110	Orange	In benzene
16	$(p\text{-}CH_3OC_6H_4Hg)_2C_6H_2(OH)(NO_2)$	Does not melt below 260°	Yellow	Insoluble
17	$(p\text{-}CH_3OC_6H_4Hg)C_6H_2(OH)(NO_2)_2$	127-129	"	In chloroform
18	$(p\text{-}CH_3OC_6H_4Hg)_2C_6H(OH)(NO_2)_2$	Does not melt below 260°	Orange	Insoluble
19	$(p\text{-}CH_3OC_6H_4Hg)C_6H(OH)(NO_2)_3$	125-126	Yellow	In alcohol and chloroform
20	$(p\text{-}CH_3OC_6H_4Hg)C_6H_3(OH)(Cl)$	154-156	White	In chloroform
21	$(p\text{-}CH_3OC_6H_4Hg)_2C_6H_2(OH)(Cl)$	Does not melt below 260°	"	Insoluble
22	$(p\text{-}CH_3OC_6H_4Hg)C_6H_2(OH)(Cl)_2$	Decomposes at 200°	Fine white	In alcohol
23	$(p\text{-}CH_3OC_6H_4Hg)C_6H(OH)(Cl)_3$	179-181	White	In benzene
24	$(p\text{-}CH_3OC_6H_4Hg)_2C_6(OH)(Cl)_3$	Does not melt below 260°	"	Insoluble
25	$(p\text{-}CH_3OC_6H_4Hg)C_6H_3(OH)_2$	169-171	Orange	In chloroform
26	$(p\text{-}CH_3OC_6H_4Hg)_2C_6H(OH)_3$	Does not melt	Fine yellow	Insoluble
27	$(p\text{-}CH_3OC_6H_4Hg)_2C_6H_2(OH)(CH_3)$	Does not melt below 250°	White regular prisms	In chloroform
28	$(p\text{-}CH_3OC_6H_4Hg)_3C_6H_2(OH)$	208	Large white prisms	In benzene
29	$(m\text{-}NO_2C_6H_4Hg)C_6H_3(OH)(NO_2)$	238-240	Orange	In pyridine
30	$(m\text{-}NO_2C_6H_4Hg)C_6H_2(OH)(NO_2)_2$	253-254	Yellow	In benzene
31	$(m\text{-}NO_2C_6H_4Hg)C_6H(OH)(NO_2)_3$	Does not melt below 250°	Pink	Insoluble
32	$(m\text{-}NO_2C_6H_4Hg)C_6H_2(OH)(Cl)_2$	151-153	Dark red	In chloroform
33	$(m\text{-}NO_2C_6H_4Hg)C_6H(OH)(Cl)_3$	Does not melt below 260°	Pink	Insoluble
34	$(m\text{-}NO_2C_6H_4Hg)_2C_6H_2(OH)_2$	Does not melt below 260°	Yellow	Ditto
35	$(m\text{-}NO_2C_6H_4Hg)C_6H_2(OH)(Cl)_2$	Does not melt below 250°	Dark yellow	Insoluble
36	$(o\text{-}NO_2C_6H_4Hg)C_6H_3(OH)(NO_2)$	187-188	Fine yellow	In benzene
37	$(o\text{-}NO_2C_6H_4Hg)C_6H_2(OH)(NO_2)_2$	196-197	Light yellow	In benzene and petroleum ether
38	$(o\text{-}NO_2C_6H_4Hg)C_6H(OH)(NO_2)_3$	181-183	Yellow	In petroleum ether
39	$(o\text{-}NO_2C_6H_4Hg)_2C_6H_2(OH)(Cl)$	Does not melt below 260°	Brown	Insoluble
40	$(o\text{-}NO_2C_6H_4Hg)C_6H_2(OH)(Cl)_2$	148	White	In benzene
41	$(o\text{-}NO_2C_6H_4Hg)C_6H(OH)(Cl)_3$	210-211	"	Ditto
42	$(o\text{-}NO_2C_6H_4Hg)_2C_6H_2(OH)_2$	Does not melt below 250°	Pink	Insoluble
43	$(o\text{-}NO_2C_6H_4Hg)C_6H_3(OH)(CH_3)$	185	Yellow	In ether
44	$(m\text{-}NO_2C_6H_4Hg)_2C_6H_2(OH)(Cl)$	Does not melt below 260°	Pink	Insoluble

SUMMARY

1. It was shown that diaryl mercury compounds of general formula $(RC_6H_4)_2Hg$ ($R = NH_2$, NO_2, OCH_3, and OH) are able to mercurate phenols at 70-150° with formation of mono-, di-, and tri-mercurated compounds.

2. The rate of mercuration and the composition of the products vary with the nature of the substituents present in the organomercury compound and in the phenol.

3. With respect to reactivity the compounds $(RC_6H_4)_2Hg$ can be arranged in the series:

$$(p\text{-}H_2NC_6H_4)_2Hg > (o\text{-}HOC_6H_4)_2Hg > (p\text{-}CH_3OC_6H_4)_2Hg > (m\text{-}NO_2C_6H_4)_2Hg >$$
$$> (o\text{-}NO_2C_6H_4)_2Hg > (p\text{-}HOOCC_6H_4)_2Hg$$

4. Phenols having substituents of the "first kind" (p-cresol, resorcinol, chlorophenols) are mercurated more readily than phenols having substituents of the "second kind" (nitrophenols).

5. A free-radical mechanism is proposed for the mercuration of phenols by mercury compounds of formula $(RC_6H_4)_2Hg$.

LITERATURE CITED

[1] O. Dimroth, Ber. 35, 2855 (1902).

[2] M.M. Koton and T.M. Zorina, J. Gen. Chem. 17, 1220, 1303 (1947); M.M. Koton and A.A. Bolshakova, J. Gen. Chem. 18, 1290 (1948); M.M. Koton, J. Gen. Chem. 19, 730, 734 (1949) (T.p. 703, 709)*; M.M. Koton and I.A. Chernov, J. Gen. Chem. 19, 2104 (1949) (T.p. a-175)*; M.M. Koton, J. Gen. Chem. 20, 2096 (1950) (T.p. 2171)*.

[3] M.M. Koton and T.M. Zorina, J. Gen. Chem. 17, 1220 (1947).

[4] M.M. Koton and V.F. Martynova, J. Gen. Chem. 25, 594 (1955) (T.p. 565)*.

[5] M.M. Koton and V.F. Martynova, J. Gen. Chem. 25, 705 (1955) (T.p. 673)*.

---

*T.p. = C.B. Translation pagination

Received December 20, 1954

Institute of Macromolecular Compounds of the USSR Academy of Sciences

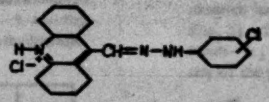
BLANK
PAGE

ABSORPTION SPECTRA AND MOLECULAR STRUCTURE

COMMUNICATION 5. SPECTROSCOPIC INVESTIGATIONS OF SOLUTIONS OF CHLORINE-SUBSTITUTED PHENYLHYDRAZONES OF 9-ACRIDINECARBOXALDEHYDE HYDROCHLORIDE IN ALCOHOLIC HYDROGEN CHLORIDE *

A.A. Kharkharov

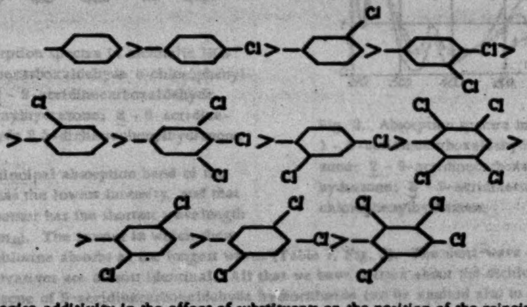
We have shown previously that as the degree of substitution of chlorine derivatives of aniline is increased the position of the principal absorption maximum, measured in alcoholic solution, is displaced in the direction of the longer waves. We found also that departures from additivity in the effects of the substituents were comparatively small for chlorine, the extent of the discrepancy being dependent on the number and positions of the substituents [1]. These conclusions have now been shown to be valid for the ultraviolet and visible spectra of solutions of chlorine-substituted phenylhydrazones of 9-acridinecarboxaldehyde hydrochloride in alcoholic hydrogen chloride:



The introduction of chlorine and other electron-accepting substituents [2] into the molecule of this compound is accompanied not by deepening of color, as was found for aniline, but by lightening. With respect to the hypsochromic effect of the halogen, monochloro derivatives fall into the order (Fig. 1, Table 1) corresponding to the demands of the inductive effect of the substituent [3]:

ortho > meta > para

In the present investigation we have found a regular displacement of the principal absorption maximum in the direction of the shorter waves as the number of substituents increase, the sequence being as follows:



Again, precise additivity in the effect of substituents on the position of the principal absorption band was scarcely ever observed, and our attention is drawn once more to the profound significance of the Butlerov-Markovnikov dialectical thesis relating to the mutual effects of atoms and of groups of atoms.

---

* Work carried out in fulfilment of requirements for the doctorate of the Institute of Organic Chemistry of the USSR Academy of Sciences.

EXPERIMENTAL*

The spectrum investigations were carried out over the range 210-700 mμ with an SF-1 photoelectric spectrophotometer. The solvent used was 0.2 N alcoholic HCl, and effects due to solvent were excluded. The measurements were made on dye solutions of identical concentration. All of the substances were prepared under the conditions that we have used previously for the preparation of 9-acridinecarboxaldehyde phenylhydrazone [4-6]. Their purities were checked by combustion analysis for nitrogen (Table 1).

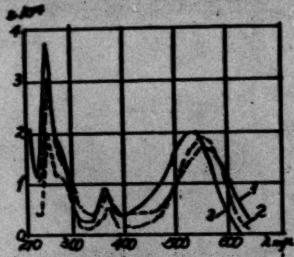


Fig. 1. Absorption spectra in alcoholic HCl: 1 - 9-acridinecarboxaldehyde p-chlorophenylhydrazone; 2 - 9-acridinecarboxaldehyde m-chlorophenylhydrazone; 3 - 9-acridinecarboxaldehyde o-chlorophenylhydrazone

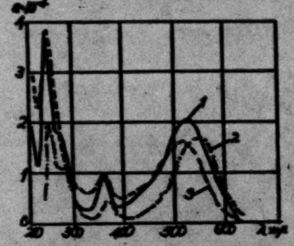


Fig. 2. Absorption spectra in alcoholic HCl: 1 - 9-acridinecarboxaldehyde o-chlorophenylhydrazone; 2 - 9-acridinecarboxaldehyde m-chlorophenylhydrazone; 3 - 9-acridinecarboxaldehyde 2,5-dichlorophenylhydrazone

The principal absorption maxima of the o-, m-, and p-chlorophenylhydrazones of 9-acridinecarboxaldehyde lie at 533, 548, and 554 mμ, respectively.

Of the three dichloro derivatives that we examined, the 2,5-isomer showed the greatest departure from additivity (−9 mμ, Table 1, Fig. 2). For the 2,4-isomer, the departure from the calculated value of the displacement of the principal absorption maximum is only 2mμ (Table 1, Fig. 3). For the 3,4-isomer, the experimentally found and calculated values of the wavelength at the principal absorption maximum coincide (Table 1, Fig. 4). The introduction of two halogen atoms into the molecule of 9-acridinecarboxaldehyde phenylhydrazone hydrochloride has little effect on the form of the curve (Fig. 5). The relative intensities of the absorption bands – $\epsilon_1 > \epsilon_3 > \epsilon_2$ – are maintained. The intensity of the principal maximum is reduced.

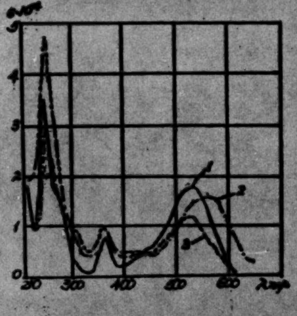


Fig. 3. Absorption spectra in alcoholic HCl: 1 - 9-acridinecarboxaldehyde p-chlorophenylhydrazone; 2 - 9-acridinecarboxaldehyde o-chlorophenylhydrazone; 3 - 9-acridinecarboxaldehyde 2,4-dichlorophenylhydrazone

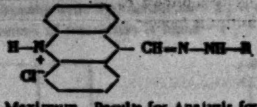
The principal absorption band of the 2,4-isomer has the lowest intensity, and that of the 2,5-isomer has the shortest wavelength (Δλ = − 52 mμ). The isomer in which there is no ortho chlorine absorbs at the longest waves (Table 1, Fig. 5). The short-wave absorption bands of the dichloro derivatives are almost identical. All that we have written about the dichloro derivatives of the phenylhydrazone of 9-acridinecarboxaldehyde hydrochloride can be applied also to the trichloro derivatives (Table 1, Fig. 6). Introduction of the three halogen atoms in the 2,4,5-positions displaces the principal maximum to a greater extent (Δλ = − 52 mμ, Table 1, Fig. 6) than their introduction into the 3,4,5-positions (Δλ = − 37 mμ, Table 1, Fig. 7). For both isomers the departure from additivity is very slight - only - 1 mμ Table 1, Fig. 6).

---

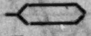
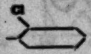
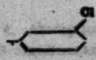
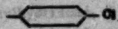
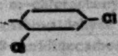
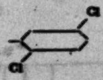
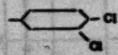
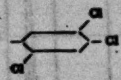
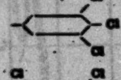
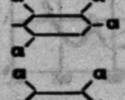
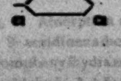
* See footnote on page 988 before the summary.

TABLE 1

Additivity of the Effects of Chlorine Atoms in Chlorine-substituted Phenylhydrazones of 9-Acridinecarboxaldehyde Hydrochloride



on the Position of the Principal Maximum. Results for Analysis for Nitrogen

R	Principal absorption maximum (mμ)	Displacement of maximum		Departure from additivity (mμ)	Molecular formula	Nitrogen content (%)	
		Observed (mμ)	Calculated (mμ)			Found	Calculated
	562	0	—	—	$C_{20}H_{15}N_3$	14.4	14.1
	533	—29	—	—	$C_{20}H_{14}N_3Cl$	12.8	12.7
	548	—14	—	—	$C_{20}H_{14}N_3Cl$	12.6	12.7
	554	— 8	—	—	$C_{20}H_{14}N_3Cl$	12.0	12.7
	523	—39	—37	— 2	$C_{20}H_{13}N_3Cl_2$	11.9	11.5
	510	—52	—43	— 9	$C_{20}H_{13}N_3Cl_2$	11.8	11.5
	540	—22	—22	0	$C_{20}H_{13}N_3Cl_2$	11.9	11.5
	510	—52	—51	— 1	$C_{20}H_{12}N_3Cl_3$	10.8	10.5
	525	—37	—36	— 1	$C_{20}H_{12}N_3Cl_3$	10.7	10.5
	509	—53	—80	+27	$C_{20}H_{11}N_3Cl_4$	9.8	9.6
	512	—50	—86	+36	$C_{20}H_{11}N_3Cl_4$	9.8	9.6

When the number of halogen atoms in the molecule is increased further, a considerable departure from additivity occurs — a transition from a quantitative to a qualitative effect. For the 2,3,4,6-tetrachloro derivative the departure from additivity is + 27 mμ (Table 1, Fig. 9). It is probable that it is at this point that a great disturbance of the planar configuration of the molecule occurs. Increase in the number of halogen atoms is accompanied by a great change in the intensity of the principal absorption band. The sequence of intensities of the absorption bands characteristic for the unsubstituted phenylhydrazone of 9-acridinecarboxaldehyde hydrochloride — $\varepsilon_1 > \varepsilon_3 > \varepsilon_2$ — breaks down for the tetrahalo derivatives; a different sequence of intensities is found — $\varepsilon_1 > \varepsilon_2 > \varepsilon_3$ (Figures 8 and 9).

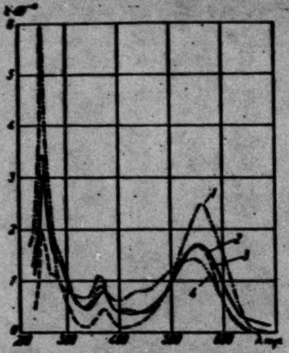


Fig. 4. Absorption spectra in alcoholic HCl: 1 - 9-acridinecarboxaldehyde 3,4-dichlorophenylhydrazone; 2 - 9-acridinecarboxaldehyde m-chlorophenylhydrazone; 3 - 9-acridinecarboxaldehyde p-chlorophenylhydrazone; 4 - 9-acridinecarboxaldehyde phenylhydrazone.

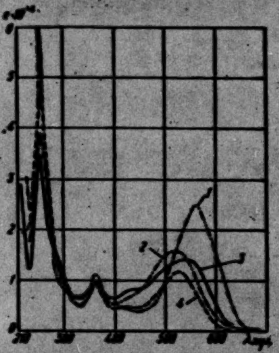


Fig. 5. Absorption spectra in alcoholic HCl: 1 - 9-acridinecarboxaldehyde 3,4-dichlorophenylhydrazone; 2 - 9-acridinecarboxaldehyde 2,4-dichlorophenylhydrazone; 3 - 9-acridinecarboxaldehyde 2,5-dichlorophenylhydrazone; 4 - 9-acridinecarboxaldehyde phenylhydrazone.

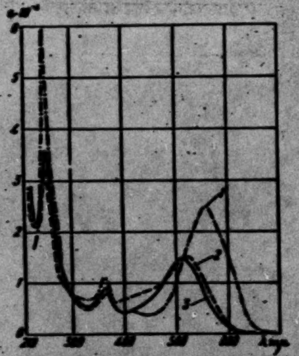


Fig. 6. Absorption spectra in alcoholic HCl: 1 - 9-acridinecarboxaldehyde 2,4,5-trichlorophenylhydrazone; 2 - 9-acridinecarboxaldehyde 3,4,5-trichlorophenylhydrazone; 3 - 9-acridinecarboxaldehyde phenylhydrazone

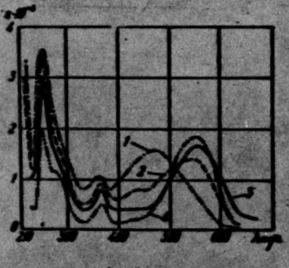


Fig. 7. Absorption spectra in alcoholic HCl: 1 - 9-acridinecarboxaldehyde 3,4,5-trichlorophenylhydrazone; 2 - 9-acridinecarboxaldehyde 3,4-dichlorophenylhydrazone; 3 - 9-acridinecarboxaldehyde m-chlorophenylhydrazone; 4 - 9-acridinecarboxaldehyde p-chlorophenylhydrazone.

TABLE 2

Principal Properties of New Chloro Derivatives of the Phenylhydrazone of 9-Acridinecarboxaldehyde Hydrochloride

No.	Name of Compound	M.p. (°C)	Color of dry substance		Color of solution					Principal absorption maximum mμ		
			in free state	as salt with acid	in aqueous alcoholic caustic soda	in alcohol	in alcoholic caustic soda	in concentrated sulfuric acid	in glacial acetic acid	in alcohol	in 0.2 N alcoholic HCl	in glacial acetic acid
1	9-Acridinecarboxaldehyde, o-chlorophenylhydrazone	210	y	r-black	y	y	y-g	y	r-v	440	533	530
2	9-Acridinecarboxaldehyde, m-chlorophenylhydrazone	218	y	v-black	o	o	y-g	y	r-v	450	548	550
3	9-Acridinecarboxaldehyde 2,4-dichlorophenylhydrazone	175	y	black	y	y	g	g-x	r	437	523	525
4	9-Acridinecarboxaldehyde 2,5-dichlorophenylhydrazone	210	y-br	g-black	y	y	g-br	g-br	r	430	510	510
5	9-Acridinecarboxaldehyde 3,4-dichlorophenylhydrazone	192	y-br	g-black	y	y	g-br	g-br	r	445	540	540
6	9-Acridinecarboxaldehyde 2,4,5-trichlorophenylhydrazone	172	br	g-black	y	y	—	br	r	—	510	510
7	9-Acridinecarboxaldehyde 3,4,5-trichlorophenylhydrazone	238	y-br	r-black	y	y	blue	y-g	r	440	525	525
8	9-Acridinecarboxaldehyde 2,3,4,6-tetrachlorophenylhydrazone	142	br	—	y	y	br	g-br	r	—	509	510
9	9-Acridinecarboxaldehyde 2,3,5,6-tetrachlorophenylhydrazone	155	br	—	y	y	o	br	r	—	512	510

Abbreviations: y - yellow; g - green;
r - red; br - brown
o - orange; v - violet

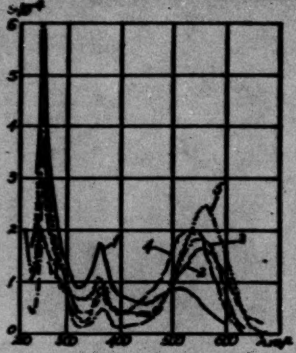


Fig. 8. Absorption spectra in alcoholic HCl: 1 - 9-acridinecarboxaldehyde 2,3,4,6-tetrachlorophenylhydrazone; 2 - 9-acridinecarboxaldehyde p-chlorophenylhydrazone; 3 - 9-acridinecarboxaldehyde m-chlorophenylhydrazone; 4 - 9-acridinecarboxaldehyde o-chlorophenylhydrazone; 5 - 9-acridinecarbonaldehyde phenylhydrazone

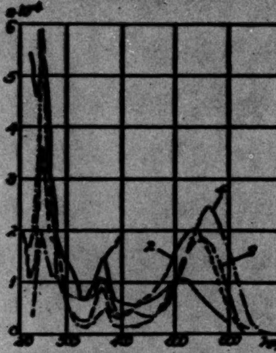


Fig. 9. Absorption spectra in alcoholic HCl; 1 - 9-acridinecarboxaldehyde 2,3,5,6-tetrachlorophenylhydrazone; 2 - 9-acridinecarboxaldehyde o-chlorophenylhydrazone; 3 - 9-acridinecarboxaldehyde m-chlorophenylhydrazone; 4 - 9-acridinecarboxaldehyde phenylhydrazone.

Comparison of the positions of the principal absorption maxima of the isomeric tetrachloro derivatives shows that four halogen atoms in the 2,3,4,6-positions have a more powerful hypsochromic effect (Δλ = − 53 mμ, Table 1) than four halogens in the 2,3,5,6-positions (Δλ = − 50 mμ, Table 1). Analogous regularities are observed for bromo, iodo, sulfo, nitro, carboxy, methyl, methoxy, and other derivatives of the phenylhydrazone of 9-acridinecarboxaldehyde hydrochloride.

The principal properties of the new chloro derivatives of the phenylhydrazone of 9-acridinecarboxaldehyde hydrochloride are given together with results of analysis for nitrogen in Tables 1 and 2.

---

*There are discrepancies between the absorption graphs and the information given in Table 1 and the text. For example, it would appear that the curves labeled 1 in Figures 4, 5, and 6 all refer to unsubstituted 9-acridinecarboxaldehyde phenylhydrazone and not to the various substances indicated below the graphs. No attempt has been made to correct the labeling. - Publisher.

SUMMARY

1. The absorption spectra of solutions of mono-, di-, tri-, and tetra-chloro derivatives of the phenylhydrazone of 9-acridinecarboxaldehyde hydrochloride in alcoholic hydrogen chloride were investigated.

2. It was shown that, with respect to the hypsochromic effects of their halogen atoms, the monochloro derivatives fall into the sequence corresponding to the demands of the inductive effect of the substituent.

3. The presence of the substituents has little effect on the general shape of the curve and the positions of the short-wave absorption maxima. As the number of substituents increases, there is a regular displacement of the principal absorption maximum in the direction of the short waves. The effects of the substituents are approximately additive.

4. It can be inferred from the behavior of the chlorine derivatives of the phenylhydrazone of 9-acridinecarboxaldehyde hydrochloride that complete additivity of the effects of substituents is practically never observed. This fact is to be attributed to the mutual effects of atoms.

5. Nine new chloro derivatives of 9-acridinecarboxaldehyde phenylhydrazone were prepared.

LITERATURE CITED

[1] A.A. Kharkharov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 5, 854.

[2] A.A. Kharkharov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 5, 880.

[3] A.N. Terenin, V.N. Kondratyev, I.L. Knunyants, M.I. Kabachnik, N.D. Sokolov, and O.A. Reutov, State of the Theory of Chemical Structure in Organic Chemistry, Acad. Sci. USSR Press, p. 66.

[4] A.E. Porai-Koshits and A.A. Kharkharov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1944, No. 1, 39.

[5] A.E. Porai-Koshits and A.A. Kharkharov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1944, No. 2-3, 143.

[6] A.E. Porai-Koshits and A.A. Kharkharov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1944, No. 4, 243.

Received November 30, 1954.

COMPARATIVE STUDY OF THE OXIDATION REACTIONS OF PECTIC SUBSTANCES, OF CELLULOSE, AND OF THE STRUCTURAL UNITS OF THESE SUBSTANCES

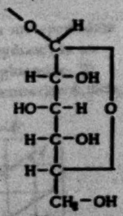
COMMUNICATION 3. COMPARATIVE STUDY OF THE REACTIVITIES OF THE STRUCTURAL UNITS OF CELLULOSE AND PECTIC SUBSTANCES IN OXIDATION REACTIONS WITH SODIUM METAPERIODATE AND HYDROGEN PEROXIDE

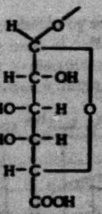
O. P. Golova and N. S. Mayat

We have shown that pectic substances present in the cotton fiber retard the oxidative degradation of cellulose which occurs when the fiber is treated with oxidizing agents in an alkaline medium. The results that we obtained can be regarded as a proof of the great tendency, relative to that of cellulose, of pectic substances to undergo oxidative degradation when these polymers occur in intimate association with the cotton fiber. This proof is a purely qualitative one and can give only a qualitative answer to the question of the relative rates at which cellulose and pectic substances present in the cotton fiber are oxidized.

It may be supposed that the difference in rate of oxidation between cellulose and pectic substances is to be attributed not only to differences in physical structure, but also to differences in chemical structure. The effect of chemical structure can be established only by a comparison of the rates of oxidation of the elementary structural units of cellulose and pectic substances, the effect of the structures of the polymers on their rates of oxidation being completely excluded. Such an investigation could be made only as the result of a comparative study of the reactivities of models of the elementary structural units of cellulose and polygalacturonic acid.

The structural unit of polygalacturonic acid differs from that of cellulose in that C-6 forms part of a carboxyl group and the hydrogen and hydroxyl at C-4 have the opposite spatial arrangement:





It may be supposed that this difference in structure between the structural units of cellulose and polygalacturonic acid will give rise to differences in reactivity and, therefore, in rates of oxidation. As approximate models of the structural units of these polymers we took methyl α-glucoside and methyl α-galactosiduronic acid, which, like the actual structural units, differ in the configuration at C-4 and in the identity of the functional group at C-6. Any difference, therefore, in the reactivities of these models can be ascribed to two causes: diastereoisomerism and the presence of a carboxyl in the one where the other has a primary alcohol group.

We made separate investigations of the effects of these two factors by making comparisons of reactivity for two pairs of model substances. We studied the effect of the first factor – diastereoisomerism – by comparing the reactivities of diastereoisomers differing only in the configuration at C-4 (methyl α-glucoside and methyl α-galactoside); and we studied the effect of the second factor – the presence of a carboxyl instead of a primary alcohol group – by comparing substances having the same configurations at all

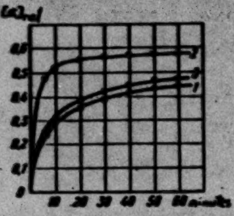


Fig. 1. Oxidation by sodium metaperiodate (2 moles per mole of carbohydrate) in an acid medium at 25°; 1) methyl α-glucoside; 2) methyl α-galactoside; 3) methyl α-galactosiduronic acid (concentration 2.5%).

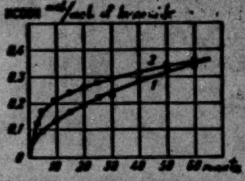


Fig. 2. Oxidation by sodium metaperiodate (2 moles per mole of carbohydrate) in an acid medium; 1) methyl α-glucoside; 2) methyl α-galactoside (concentration 0,25%).

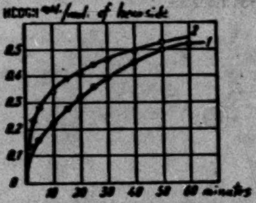


Fig. 3. Oxidation by sodium metaperiodate (4 moles per mole of carbohydrate) in an acid medium; 1) methyl α-glucoside; 2) methyl α-galactoside (concentration 0,25%).

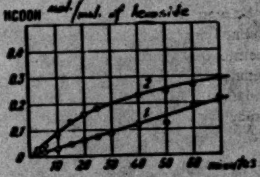


Fig. 4. Oxidation by sodium metaperiodate (4 moles per mole of carbohydrate) in an acid medium; 1) methyl α-glucoside; 2) methyl α-galactoside (concentration 0,125%).

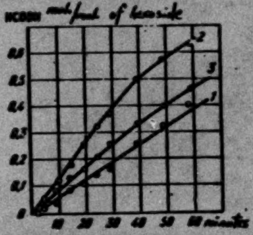


Fig. 5. Oxidation by sodium metaperiodate (4 moles per mole of carbohydrate) in an alkaline medium; 1) methyl α-glucoside; 2) methyl α-galactoside; 3) methyl α-galactosiduronic acid (concentration 0,125%).

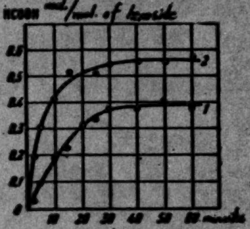


Fig. 6. Oxidation by hydrogen peroxide (4 moles per mole of carbohydrate) in an alkaline medium; 1) methyl α-glucoside; 2) methyl α-galactoside (concentration 0,25%).

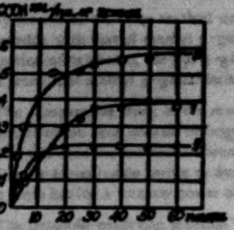


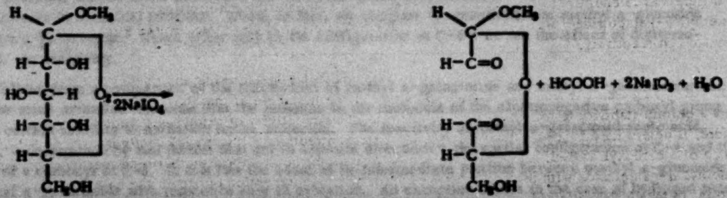
Fig. 7. Oxidation by hydrogen peroxide (4 moles per mole of carbohydrate) in an alkaline medium: 1) methyl α-glucoside; 2) methyl α-galactoside; 3) methyl α-galactosiduronic acid (concentration 0.25%).

asymetric carbon atoms but different functional groups at C-6 (methyl α-galactoside and methyl α-galactosiduronic acid).

The reactivities of these hexosides were studied in oxidation reactions with sodium metaperiodate and hydrogen peroxide under the conditions that we have used previously in a study of the degradation of pectic substances [1] (oxidation with $NaIO_4$ at 20°, and with H_2O_2 at 92°). The amount of oxidant taken for reaction was that required theoretically for complete rupture of the pyran ring, i.e. two moles of oxidant per mole of carbohydrate. In some experiments 100% excess was taken.

For the investigation of the relative reactivities of these hexosides, two methods were used: 1) polarimetry, and 2) quantitative determination of formic acid. The application of polarimetry for this purpose was possible because oxidation of these hexosides by sodium metaperiodate yields oxidation products that are of one type, or even identical, and cause the specific rotation to change in the same direction (a reduction). The reactivities of these hexosides can therefore be characterized by the relative changes in specific rotation occurring during the oxidation process.

The use of the determination of formic acid for this purpose is based on the fact that in the oxidation of these hexosides by sodium metaperiodate, one mole of hexoside gives one mole, quantitatively, of formic acid [2]. Under certain conditions (at temperatures approaching 100° and in absence of catalyst), the same relationship is preserved also in oxidation by hydrogen peroxide [3].



For the characterization of the reactivities of the hexosides toward acid solutions of sodium metaperiodate we used both methods. When using polarimetry, we determined the relative changes in the specific rotation of 2.5% aqueous solutions of the hexosides at 20° and 25°.

The results obtained at 25° are presented in Fig. 1 in the form of curves for the dependence of $[\alpha]^{20}_{D\,rel}$ on time.

These results show that, in the initial period of oxidation, methyl α-galactoside is more reactive than methyl α-glucoside. Methyl α-galactosiduronic acid occupies an intermediate position. The results were confirmed and extended by the further results obtained by the determination of formic acid, in which the reactivity of the hexoside at a given moment was characterized by the number of moles of formic acid yielded by one mole of the hexoside from the beginning of the reaction up to that moment.

The reactivities of hexosides toward sodium metaperiodate were determined both in acid (pH 4.2) and in alkaline (pH 11-12) media at 20°. In the determination of the reactivities of methyl α-glucoside and methyl α-galactoside in acid medium at various concentrations of oxidant (2 and 4 moles per mole of hexoside) and of substance undergoing oxidation, appreciable differences between the reactivities of the hexosides were always found during the whole of the time (60 minutes) for which reaction was allowed to continue (Figures 2, 3, and 4). It was found also that the reactivities of the hexosides increase with increase in concentration of oxidant and with diminution in the concentration of the substance undergoing oxidation.

By the use of the same method we compared the reactivities of methyl α-glucoside and methyl α-galactoside with that of methyl α-galactosiduronic acid in an alkaline medium. It was found that, in the initial period of oxidation, methyl α-galactosiduronic acid is more prone to oxidation than methyl α-glucoside, but less prone that methyl α-galactoside (Fig. 5).

The comparative study of the reactivities of methyl α-glucoside, methyl α-galactoside, and methyl α-galactosiduronic acid toward hydrogen peroxide was carried out only in an alkaline medium (pH 11-12) at 95°. In this case the reactivities were characterized only by formic acid determinations, the polarimetry method being inapplicable owing to the possibility of the formation of a complex mixture of products, including some having a rotatory power of opposite sign.

The hexoside-oxidation reaction was carried out at different relative concentrations of oxidant (2 and 4 moles of hydrogen peroxide per mole of hexoside undergoing oxidation) and at various concentrations of the substance undergoing oxidation. The results obtained (Fig. 6) show that, although the oxidation of the hexosides by hydrogen peroxide in an alkaline medium has, kinetically (as also chemically), a different character than their oxidation by sodium metaperiodate under the same conditions, the relative reactivities of methyl α-glucoside and methyl α-galactoside remain qualitatively the same as before: methyl α-galactoside is more readily oxidized than methyl α-glucoside.

When the reactivities of methyl α-glucoside and methyl α-galactoside are compared with that of methyl α-galactosiduronic acid, it will be seen that, in the initial period of oxidation (10-15 minutes), methyl α-galactosiduronic acid occupies an intermediate position. As oxidation proceeds further, methyl α-galactosiduronic acid becomes less reactive than methyl α-glucoside (Fig. 7). This fact was confirmed several times in comparative oxidations of methyl α-glucoside and methyl α-galactosiduronic acid at three different hexoside concentrations (0.25%, 0.125% and 0.0625%).

Hence, as a result of this comparative investigation of the reactivities of methyl α-glucoside, methyl α-galactoside, and methyl α-galactosiduronic acid in oxidation reactions with sodium metaperiodate and hydrogen peroxide, we reach the conclusion that these hexosides have different reactivities as a result of their differences in chemical structure. When, in fact, we compare the reactivities of methyl α-glucoside and methyl α-galactoside — which differ only in the configuration at C-4 — we see the effect of diastereoisomerism on reactivity.

It follows from a comparison of the reactivities of methyl α-galactoside and methyl α-galactosiduronic acid in the same oxidation reactions that the presence in the molecule of the electronegative carboxyl group confers a certain stability to oxidation on the molecule. The reactivity of methyl α-galactosiduronic acid, therefore, is determined by two factors that act in opposite directions — the spatial configuration at C-4 and the presence of a carboxyl at C-6. In this lies the cause of its intermediate position between methyl α-glucoside and methyl α-galactoside with respect to ease of oxidation. An exception occurs in the case of hydrogen peroxide oxidation, in which the difference in reactivity between methyl α-glucoside and methyl α-galactoside becomes negative. At present there is no explanation for this behavior, which requires further investigation.

It has been shown, therefore, that when oxidized by sodium metaperiodate, and also by hydrogen peroxide under defined conditions, methyl α-galactosiduronic acid is more reactive than methyl α-glucoside. This difference can be attributed to diastereoisomerism, and, together with the difference in physical structure between cellulose and pectic substances, it is the source of the difference in the rates of oxidation of the structural units, and therefore also the source of the difference in the rates of degradation of these polymers.

EXPERIMENTAL

1. Determination of Reactivity by the Polarimetry Method

Oxidation with Sodium Metaperiodate. A 0.25-g sample of the substance was dissolved in 5 ml of water and transferred quantitatively to a 10-ml measuring flask. The calculated amount of a saturated solution of sodium metaperiodate was added, and the mixture was made up to volume. The solution was mixed rapidly, and the micro-tube of the polarimeter was filled. The specific rotation was determined every 1-2 minutes for a period of 30 minutes from the start of the oxidation, and thereafter every 3-5 minutes (the start of the oxidation was taken to be the moment the sodium metaperiodate was added to the solution).

The specific rotation was calculated from the formula:

$$[\alpha]_D^{20} = \frac{\alpha}{l \cdot c} \qquad (1)$$

in which α is the angle through which the plane of polarization is turned, c is the concentration of the substance in g/cm, and l is the length of the tube (cm).

The values of $[\alpha]_D^{20}$ for the original substances were determined in a similar way. From the values of $[\alpha]_D^{20}$ the relative change in $[\alpha]_D^{20}$ was calculated from the formula:

$$[\alpha]_{D\,\mathrm{rel}}^{20} = \frac{[\alpha]_{D\,\mathrm{init}} - [\alpha]_D}{[\alpha]_{D\,\mathrm{init}} - [\alpha]_{D\,\mathrm{fin}}} \qquad (2)$$

in which $[\alpha]_{D\,\mathrm{init}}^{20}$ is the specific rotation of the unoxidized substance, $[\alpha]_{D\,\mathrm{fin}}^{20}$ is the specific rotation of the oxidized substance, and $[\alpha]_D^{20}$ is a value of the specific rotation determined during the oxidation process.

From the values of $[\alpha]_{D\,\mathrm{rel}}^{20}$ so obtained, graphs showing its variation with time were plotted (Fig. 1).

2. Determination of Reactivity by the Quantitative Determination of Formic Acid

Oxidation with Sodium Metaperiodate in an Acid Medium. An exactly weighed amount of the hexoside was dissolved in a little water (10 ml) and transferred quantitatively to a 100-ml measuring flask. The calculated amount of a saturated solution of sodium metaperiodate was added, and the mixture was shaken rapidly and placed in a thermostat at 20°. The moment at which the sodium metaperiodate was added was taken to be the time of the start of the reaction. After 3, 5, 10, 15, 20, 25, 30, 40, 50, and 60 minutes from the start of the reaction, 5 ml of the solution was transferred to a conical flask containing 10 ml of water and 0.2 ml of ethylene glycol. Addition of ethylene glycol was essential in order to destroy the excess of oxidant. The mixture was stirred for three minutes, and the formic acid present was then titrated with 0.02 N NaOH to Methyl red. At the same time, a control experiment was carried out which was identical, except that the oxidizable substance was absent; it was thus confirmed that, under the given conditions, neither ethylene glycol nor sodium metaperiodate gave an acid reaction to Methyl red.

The results of the determination were expressed as the number of moles of HCOOH yielded by one mole of the hexoside, which was calculated from the formula:

$$\frac{x \cdot a \cdot K \cdot 0.00092 \cdot M_{\mathrm{hex}}}{(\text{weight taken}) \cdot 46} \qquad (3)$$

in which x is the number of milliliters of 0.02 N NaOH required for the titration of the formic acid in 5 ml of the reaction mixture; K is the correction factor of the 0.2 N NaOH; M_{hex} is the molecular weight of the hexoside; and a is the dilution.

Oxidation with Sodium Metaperiodate in an Alkaline Medium. An exactly weighed amount of the hexoside was dissolved in a little water, and the solution was transferred quantitatively to a 100 ml measuring flask. To this mixture 10 ml of 0.1 N NaOH and the calculated amount of sodium metaperiodate were added. In other respects the procedure was the same as for the acid medium, but the amount of formic acid formed was determined by back-titration of the unneutralized alkali with 0.02 N HCl. A control experiment (no oxidizable substance) was carried out simultaneously. The amount of formic acid produced was determined from the difference in the volumes of 0.02 N HCl required for the titration of 5 ml in the control experiment and in the hexoside-oxidation experiment; it was calculated from the formula:

$$\frac{(y-x) \cdot a \cdot K \cdot 0.00092 \cdot M_{\mathrm{hex}}}{(\text{weight taken}) \cdot 46} \qquad (4)$$

in which y is the number of milliliters of 0.02 N HCl required for the titration of 5 ml of reaction mixture in the control experiment, and x is the corresponding amount for the hexoside-oxidation experiment.

As the methyl ester of methyl α-galactosiduronic acid is readily oxidized in an alkaline medium, it was first hydrolyzed by the addition of the amount of alkali necessary for complete hydrolysis, followed by standing overnight. In other respects the procedure was as before.

Oxidation with Hydrogen Peroxide in an Alkaline Medium. A weighed amount of the hexoside was dissolved in 10 ml of water, the solution was transferred to a 50-ml measuring flask, 5 ml (7.5 ml in the case of methyl α-galactosiduronic acid) of 0.1 N NaOH was added, and the mixture was set aside overnight. The required amount of hydrogen peroxide was then added, the mixture was made up to the mark with distilled water and mixed carefully, and some of it was transferred to ampoules of 3-4 ml capacity. The ampoules were placed in a thermostat at 95°, and then removed, one at a time, after 3, 5, 10, 15, 20, 25, 30, 40, 50, and 60 minutes from the start of the oxidation. Each ampoule was broken into a small beaker, and 2 ml of its contents was transferred to a small conical flask, in which the excess of alkali was titrated with 0.02 N HCl to Methyl red. A control experiment (no oxidizable substance) was carried out simultaneously. From the difference in the volumes of 0.02 N HCl required for the titration of 2 ml in the control and in the hexoside-oxidation experiments, the amount of formic acid was determined (Formula 4).

SUMMARY

1. Under the conditions studied, methyl α-galactosiduronic acid was more readily oxidized than methyl α-glucoside.

2. It was shown that the difference in the reactivities of these models, and therefore of the elementary structural units of the corresponding polymers, is determined by the difference in spatial configuration at C-4 of the pyranose ring.

LITERATURE CITED

[1] O.P. Golova, V.I. Ivanov, and N.S. Mayat, Proc. Acad. Sci. USSR 86, No. 6, 1113 (1952).

[2] E.L. Jackson, C.S. Hudson, J. Am. Soc., 59, 994, (1937); 61, 959 (1939); T.G. Halsall, E.L. Hirst, J.N. Jones, J. Chem. Soc., 1947, 427.

[3] K. Th. Küchlin, Rec. trav. chim. 51, 899 (1932); V.I. Ivanov, E.D. Kaverzneva, and Z.I. Kuznetsova, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 2, 374 (1953). (T.p. 341)*

Received December 7, 1954

Forestry Institute of the USSR Academy of Sciences

---

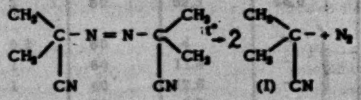
* T.p. = C.B. Translation pagination.

POLYMERIZATION OF ISOPROPYL VINYL AND CYCLOHEXYL VINYL ETHERS IN PRESENCE OF 2,2'-AZOBIS[2-METHYLPROPIONITRILE]

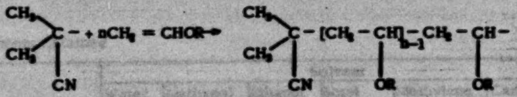
M.F. Shostakovsky, F.P. Sidelkovskaya, and E.S. Shapiro

It is known that vinyl ethers readily polymerize in presence of ionic catalysts of acidic character [1]. One of us and coworkers has recently shown that vinyl ethers are able to react also by a radical mechanism in addition and polymerization reactions. We studied the polymerization of ethyl vinyl, butyl vinyl [2], and phenyl vinyl [3] ethers in presence of 2,2'-azobis[2-methylpropionitrile]. In earlier work [4] on the addition of hydrogen sulfide to alkyl vinyl ethers it was established that ethers containing ramified and cyclic radicals show a greater tendency to react by an ionic mechanism and are more sensitive to factors that inhibit free-radical reactions.

It was considered to be of interest in this connection to investigate the polymerization of isopropyl vinyl and cyclohexyl vinyl ethers in presence of 2,2'-azobis[2-methylpropionitrile]. Initiation by the azo nitrile occurs as a result of its decomposition to form radicals [5]:



The resulting radical (I) reacts at the double bond of the vinyl ether and initiates polymerization:



The termination of the growing chain comes about as a result of either the elimination of a hydrogen atom or acetal formation.

The polymerization of cycolhexyl vinyl and isopropyl vinyl ethers was carried out in sealed tubes in presence of 0.1-5% of initiator at 40°, 60°, and 80°. The principal results obtained are shown in Table 1.

With the object of purifying the polymers, attempts were made to reprecipitate them from solution. Experiments were carried out on poly[isopropyl vinyl ether], but we were unable to bring about reprecipitation since the material is readily soluble in almost all organic solvents (Table 2). Water is a precipitant, but it precipitates the initiator at the same time.

The polymers of isopropyl vinyl ether, which were sticky viscous liquids, were therefore not purified and were not characterized further. Poly[cyclohexyl vinyl ether], like most alkyl vinyl ether polymers, is soluble in benzene and ether, but insoluble in the lower alcohols. It was therefore purified by reprecipitation with alcohol from its solution in ether. This process yielded slightly colored transparent solid polymers, which were readily ground into fine powders. In spite of the fact that the cyclohexyl vinyl ether polymers obtained were solids, their molecular weights were relatively low. However, they melted at only 47-50°.

An examination of Table 1 indicates that, under like conditions, cyclohexyl vinyl ether polymerizes much more readily than isopropyl vinyl ether. Also, the effect of temperature is more marked in the polymerization of the cyclohexyl ether: both polymers are formed in low yield at 40°, and with rise in temperature the yield of poly[cyclohexyl vinyl ether] increases appreciably, whereas that of poly[isopropyl vinyl ether] remains substantially unchanged. For both ethers there is an increase in the yield of polymer as the concentration of initiator increases.

It is very interesting to compare the reactivities of cyclohexyl vinyl and phenyl vinyl ethers (see Tables 1 and 3).

TABLE 1

Polymerization of Isopropyl Vinyl and Cyclohexyl Vinyl Ethers in presence of 2,2'-Azobis[2-methylpropionitrile] (130 hours)

Expt. No.	Ether	Amount of azo nitrile (%)	Temperature (° C)	Yield of polymer (%)		Characteristics of reprecipitated polymer		
				not reprecipitated	reprecipitated	Molecular weight	N content (%)	M. p. (° C)
1	C_6H_{11}	0	60	0.1	–	–	–	–
2	Ditto	0.1	60	13.9	10.1	1374 1440	Traces	47-48
3	"	1	60	29.4	22.0	1299 1289	Traces	47-48
4	"	1	40	12.6	–	–	–	–
5	"	1	80	25.5	–	–	–	–
6	"	3	60	49.0	40.0	1163	0.675 0.635	47-49
7	"	5	60	52.3	44.0	1124 1072	0.957 0.956	47-48
8	$i\text{-}C_3H_7$	0.1	60	4	–	Attempts to reprecipitate were not successful		
9	Ditto	1	60	11.4	–			
10	"	1	40	12.6	–			
11	"	1	80	9.2	–			

TABLE 2

Solubility of Polymers Obtained

Polymer	Solvent								
	Water	Methanol	Ethanol	Butyl alcohol	Methylene chloride	Carbon tetrachloride	Benzene	Ether	Petroleum ether
Poly[isopropyl vinyl ether]	–	+	+	+	+	+	+	+	+
Poly[cyclohexyl vinyl ether]	–	–	–	+	+	+	+	+	+

TABLE 3

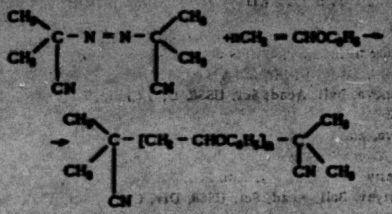
Polymerization of Phenyl Vinyl Ether in presence of 2,2'-Azobis[2-methylpropionitrile] *

Expt. No.	Amount of initiator (%)	Temperature (°C)	Time (hours)	Yield of polymer (%)	Molecular weight	N content (%)	Formula of polymer
1	1	60	280	7.2	787	2.5	$(C_8H_8O)_5C_8H_{12}N_2$
2	4	60	100	14.0	805	1.8	$(C_8H_8O)_6C_8H_{12}N_2$

---

* Results of M.F. Shostakovsky and A.V. Bogdanova [3].

These results show that, in presence of 2,2'-azobis[2-methylpropionitrile], cyclohexyl vinyl ether polymerizes more readily than phenyl vinyl ether. In the latter case the authors concluded [3] that the azo nitrile not only activates the polymerization of the ether, but also terminates it, so that the polymer is built up from 5-6 molecules of phenyl vinyl ether and two residues of the azo nitrile [the radical (I)]:



(n = 5 or 6).

This phenomenon was not observed in the polymerization of cyclohexyl vinyl ether. The nitrogen content of the polymer is very low (Table 1), and, although the nitrogen content increases somewhat with increase in the concentration of initiator, it remains too low to provide a basis for any definite conclusions (in view of the accuracy with which the analysis can be made). Hence, the character of the polymerization and chain-termination processes is somewhat different for cyclohexyl vinyl ether than for phenyl vinyl ether–a fact that is to be explained mainly by the absence of double bonds in the ring.

In a comparison of free-radical polymerization (in presence of the azo nitrile) and ionic polymerization (in presence of $FeCl_3 \cdot 6H_2O$), as observed in isopropyl vinyl and cyclohexyl vinyl ethers, it should be noted that in free-radical polymerization the yields and molecular weights of the polymers are lower than in ionic polymerization. In the latter case the yield of poly[isopropyl vinyl ether] is about 60% and its molecular weight is 4500 and the yield of cyclohexyl vinyl ether is about 96% and its molecular weight is 1500 [6]; also both polymers are viscous liquids. On the other hand, as already pointed out, in the polymerization of cyclohexyl vinyl ether in presence of the azo nitrile, brittle solid polymers are obtained, in spite of the fact that their molecular weights do not exceed 1300. This peculiar behavior is evidently associated, on the one hand, with the nature of the original monomer and, on the other, with the character of the initiation of the polymerization process. It follows from the above that vinyl ethers, when polymerized by the free-radical mechanism in presence of 2,2'-azobis[2-methylpropionitrile], give polymers of comparatively low molecular weight, the yields and properties of these polymers being dependent on the structure of the vinyl ether used.

EXPERIMENTAL

The starting materials were 1) isopropyl vinyl ether, a commercial product purified by the standard procedure of the Vinyl Compounds Laboratory, b.p. 55-56°, n_D^{20} 1,3860; 2) cyclohexyl vinyl ether, prepared by the vinylation of cyclohexanol in an autoclave by Favorsky and Shostakovsky's method, b.p. 42° (11 mm), n_D^{20} 1.5180 [7]; and 3) 2,2'-azobis[2-methylpropionitrile], which was purified by recrystallization from methanol.

Weighed amounts of catalyst and vinyl ether (20-30 g) were placed in a tube, which was sealed and heated in a thermostat for the required period of time. The tubes were then cooled and opened, and their contents were vacuum-distilled in order to remove monomer. For cyclohexyl vinyl ether, the evacuation was carried out at a residual pressure of 5-6 mm until the residual polymer attained constant weight (the bath temperature was not allowed to exceed that used in the polymerization experiment). The reaction product obtained from isopropyl vinyl ether was first evacuated to 30-40 mm in order to remove most of the monomer, and the residual polymer was dried to constant weight at 5-6 mm. The principal results obtained are given in Table 1. Polymers No. 2,3,6, and 7 were reprecipitated, for which purpose they were dissolved in ether (15 g of polymer in 10 ml of ether) and precipitated with ethanol (150 ml to 10 ml of ether). The precipitated polymer was separated, washed twice with alcohol, and vacuum-dried to constant weight at 60°.

SUMMARY

1. A study was made of the free-radical polymerization of cyclohexyl vinyl and isopropyl vinyl ethers in presence of 2,2'-azobis[2-methylpropionitrile].

2. It was shown that the yields and molecular weights of the resulting polymers are dependent on the conditions of polymerization and the structure of the ether.

LITERATURE CITED

[1] M.F. Shostakovsky, Vinyl Ethers, Acad. Sci. USSR Press, Moscow, 1952.

[2] M.F. Shostakovsky, Problems Relating to the Mechanisms of Organic Reactions, Ukrainian SSR Acad. Press, Kiev, 1954, p. 180.

[3] M.F. Shostakovsky and A.V. Bogdanova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No. 5, 911 (T.p. 789)*.

[4] M.F. Shostakovsky, E.N. Prilezhaeva, and E.S. Shapiro, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No. 2, 303 (T.p. 265)*.

[5] C.G. Overberger, M.T. O'Shaughnessy a. H. Shalit, J. Am. Soc. 71, 2661 (1949).

[6] M.F. Shostakovsky and B.I. Mikhantyev, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, No. 6, 1056 (T.p. 939)*.

[7] M.F. Shostakovsky, N.A. Gershtein, Ya. L. Raskin, and L.E. Ostroumova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1952, No. 3, 471 (T.p. 453)*.

Received December 29, 1954

N.D. Zelinsky Institute of Organic Chemistry of the
USSR Academy of Sciences

---

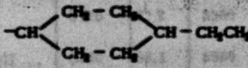
* T.p. = C.B. Translation pagination.

MACROMOLECULAR COMPOUNDS

COMMUNICATION 83. SYNTHESIS OF POLYALKYLENECYCLOALKYLS

V.V. Korshak and G.S. Kolesnikov

No macromolecular compounds are yet known which have linear molecules consisting of alternating alkane and cycloalkane residues, i.e. of the general type $C_nH_{2n-2}C_mH_{2m}$, for example:



Such macromolecular carbon-chain compounds containing cyclohexane residues as have been prepared have contained these residues as side chains, not as components of the polymer chain. Such compounds include polymers of vinylcyclohexane, prepared by the hydrogenation of polystyrene [1, 2].

The preparation of macromolecular compounds having chains composed of cycloalkane and alkane residues can be effected by several methods, but all of these are very complex and consist of many stages. It is probably for this reason that no attempts have yet been made to synthesize such compounds. However, macromolecular compounds of this type can be prepared in one stage by the hydrogenation of the corresponding polyalkylenearyls. This method for the synthesis of a new class of macromolecular compounds – polyalkylenecycloalkyls – has not been suggested previously, and we therefore undertook the task of synthesizing polyalkylenecycloalkyls by this method.

In order to determine whether polyalkylenearyls can be hydrogenated like other aromatic hydrocarbons in presence of Raney nickel without being degraded, we carried out a series of experiments on the hydrogenation of various polyalkylenearyls prepared by the polycondensation of dihaloalkanes with aromatic hydrocarbons in presence of aluminum chloride and by the transarylation of diarylalkanes [3, 4].

The hydrogenation of polyalkylenearyls was carried out in cyclohexane and in mixtures of cyclohexane and benzene. It was shown also that the hydrogenation can be carried out in absence of solvent. The catalyst was prepared by the leaching of a nickel-aluminum alloy [5], and it was preserved in jars under alcohol. A definite volume of slurry, consisting of catalyst and alcohol, was taken for the hydrogenation. The following substances were hydrogenated:
poly[methylenephenyl] $(CH_2C_6H_4)n$, poly[ethylenephenyl] $(CH_2CH_2C_6H_4)n$, poly[ethylenetolyl] $(CH_2CH_2C_6H_3(CH_3))n$, poly[ethylenebiphenylyl] $(CH_2CH_2C_6H_4C_6H_4)n$, poly[ethylenenaphthyl] $(CH_2CH_2C_{10}H_6)n$, and poly[ar-ethylene-1,2,3,4-tetrahydronaphthyl] $(CH_2CH_2C_{10}H_{10})n$. The results obtained are given in Table 1.

Table 1 shows that polyalkylenearyls usually undergo hydrogenation in presence of Raney nickel, and for some of them (Experiments 2 and 3) hydrogenation is almost complete. The causes of incomplete hydrogenation may be the presence of impurities in the polyalkylenearyls and the use of hydrogenation conditions that did not correspond to the optimum conditions for the process.

The hydrogenation of poly[ethylenephenyl] can be represented by the scheme:

$$(CH_2CH_2C_6H_4)_n + 3nH_2 \xrightarrow{Ni} (CH_2CH_2C_6H_{10})_n.$$

and the hydrogenation of the other polyalkylenearyls proceeds similarly.

The products formed by the hydrogenation of polyalkylenearyls are macromolecular compounds, and they preserve the original appearance, apart from color. The color of the hydrogenation products is not so deep as that of the polyalkylenearyls from which they are derived, and when hydrogenation is complete, or almost complete, the products are light yellow, or even only slightly yellowish.

TABLE 1

Hydrogenation of Polyalkylenearyls

Expt. No.	Polyalkylenearyl	Molecular weight	Hydrogenation product		Content (%)			
			Yield (%)	Molecular weight	Found		Calculated for poly[alkylenecycloalkyl]	
					C	H	C	H
1	Poly[methylenephenyl]	1420	93.4	1620	88.27 88.35	11.27 11.37	87.43	12.57
2	Poly[ethylenephenyl]	2560	87.8	2890	87.19 87.40	12.82 12.94	87.19	12.81
3	Poly[ethylenetolyl]	3120	93.2	3300	87.45 87.30	12.32 12.60	87.02	12.98
4	Poly[ethylenebiphenylyl]	3540	88.1	3500	88.55 88.42	11.67 11.50	87.42	12.58
5	Poly[ar-ethylene-1,2,3,4-tetrahydronaphthyl]	2940	82.7	2900	88.66 88.55	11.45 11.45	87.79	12.21
6	Poly[ethylenenaphthyl]	2460	64.4	2540	89.77 90.08	9.88 9.89	87.79	12.21

It is interesting that the lightening of the color of polyalkylenearyls during hydrogenation occurs more rapidly than the growth in the extent of the hydrogenation. We attempted to estimate quantitatively the change in color occurring during the hydrogenation of polyalkylenearyls, and for this purpose we compared the colors of benzene solutions of some polyalkylenearyls with the same solutions after the hydrogenation treatment, the comparison being made with the aid of a Duboscq colorimeter.

If the change produced by hydrogenation in the intensity of the color of the polyalkylenearyl were directly proportional to the extent of hydrogenation of the aromatic cycles, then the following equation would hold:

$$c_1 \cdot h_1 = c_2 \cdot h_2 \cdot A,$$

in which c_1 is the concentration of the solution of polyalkylenearyl (basal moles per liter), h_1 is the thickness of the layer of polyalkylenearyl solution (mm), c_2 is the concentration of the solution of hydrogenated polyalkylenearyl (basal moles per liter), h_2 is the thickness of the layer of the solution of hydrogenated polyalkylenearyl, and A is a coefficient expressing the fraction of the originally aromatic cycles of the polyalkylenearyl that remain unhydrogenated. The coefficient A has the value

$$A = \frac{\Delta H_t - \Delta H}{\Delta H_t}$$

in which ΔH_t is the total change in the hydrogen content of the repeating unit of the polyalkylenearyl when it is completely hydrogenated (%), and ΔH is the observed change in the hydrogen content of the repeating unit during the hydrogenation of the polyalkylenearyl (%).

As the change in the molecular weight of the repeating unit of the polyalkylenearyl resulting from hydrogenation – particularly partial hydrogenation – is not great, c_1 and c_2 can be expressed in grams per liter for a given polyalkylenearyl. Table 2 gives values of

$$c_1 \cdot h_1;\ c_2 \cdot h_2 \cdot A \quad \text{and} \quad \frac{c_2 \cdot h_2 \cdot A}{c_1 \cdot h_1},$$

calculated from the results of the colorimetric measurements. It will be seen from Table 2 that in no case is the equation $c_1 \cdot h_1 = c_2 \cdot h_2 \cdot A$ observed, which indicates the absence of direct proportionality between the intensity of the color and the extent of the hydrogenation of the aromatic cycles. We consider that the results obtained can be explained as follows. It is known that, when we pass from aromatic compounds to cycloalkanes formed from them by hydrogenation, there is a shift in the absorption spectrum toward the shorter waves. It may be expected that the conversion of phenylene groups into cyclohexylene groups will also result in a shift in the absorption spectrum toward the shorter waves.

TABLE 2

Change in Color resulting from the Hydrogenation of Polyalkylenearyls*

Polyalkylenearyl	A	$c_1 \cdot h_1$	$c_2 \cdot h_2 \cdot A$	$\frac{c_2 \cdot h_2 \cdot A}{c_1 \cdot h_1}$
Poly[methylenephenyl]	0.28	7.0	114.4	16.3
Poly[ethylenephenyl]	0.50	11.5	21.3	1.85
Poly[ethylenetolyl]	0.79	17.3	289.3	16.7
Poly[ethylenebiphenylyl]	0.17	4.1	87.4	21.3
Poly[ethylenenaphthyl]	0.43	1.9	283.4	149.2

---

* Partial-hydrogenation products of polyalkylenearyls were taken for the measurements.

Comparison of the absorption spectra of poly[ethylenephenyl] and its hydrogenation product poly-[ethylenecyclohexyl] (Figures 1 and 2) shows that hydrogenation causes the spectrum to be displaced considerably toward the ultraviolet region*. Hence, the replacement of phenylene by cyclohexylene results in a change in the absorption spectrum of the polymer. It is probable that the color of poly-[ethylenephenyl] and other polyalkylenearyls is the result of the accumulation of a large number of phenylene groups in the polymer chain. This supposition was to a certain extent confirmed by comparison of the absorption spectra of bibenzyl and diphenethylbenzene (Figures 3 and 4); these compounds were obtained by us among the products of the polycondensation of 1,2-dichloroethane with benzene in presence of aluminum chloride [3, 6]. It will be seen from Fig. 4 that replacement of a hydrogen of the phenyl radical by the phenethyl radical results in an appreciable shift of the absorption spectrum toward the nearer ultraviolet region.

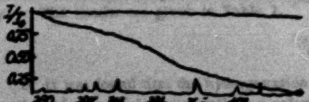


Fig. 1. Absorption spectrum of poly-[ethylenephenyl]

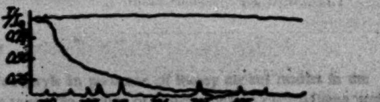


Fig. 2. Absorption spectrum of poly-[ethylenecyclohexyl]

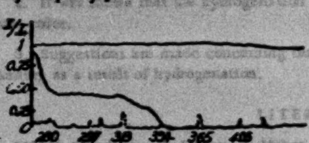


Fig. 3. Absorption spectrum of bibenzyl

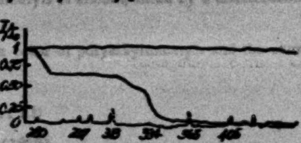
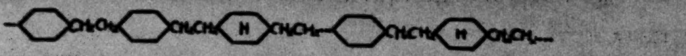


Fig. 4. Absorption spectrum of diphenethylbenzene

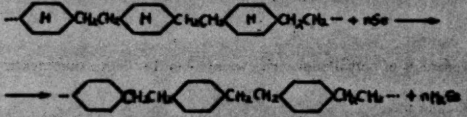
---

* The absorption spectra given in this paper were determined by L.A. Palitsina, to whom we express our sincere thanks.

It is probable that the change in color associated with change in the nature of part of the polyalkylenearyl molecule (when hydrogenation is partial) may be related to the extent of hydrogenation in accordance with a law that is more complex than direct proportionality. The hydrogenation of individual phenylene groups in the polyalkylenearyl molecule may result in the partition of the polyalkylenearyl chain by cyclohexylene groups, or catenations of such groups, into short polyalkylenearyl chains. In this way the mutual effects of the phenylene groups within the chain – which are the source of the color – will be weakened, or even rendered quite ineffective.



It is known that the lower members of this polymer-homologous series are not colored at all, or are very feebly colored (diphenylmethane, diphenylethane, diphenethylbenzene, and others) and the partition of the polyalkylenearyl molecule into short chains will probably result in a considerable weakening of the color, since such a molecule of irregular structure can be regarded as the sum of the individual short molecules (only from a point of view of color). Dehydrogenation of the hydrogenation product from poly[ethylenephenyl] by means of selenium gave the original poly[ethylenephenyl], which yielded terephthalic acid when oxidized. The terephthalic acid was identified as the dimethyl ester.



EXPERIMENTAL

The polyalkylenearyls were hydrogenated in an electrically heated two-liter stainless-steel rotating autoclave. The polyalkylenearyl to be hydrogenated was dissolved in cyclohexane or a mixture of cyclohexane and benzene, the solution was poured into the autoclave, and Raney nickel was added in the form of a slurry with alcohol. The autoclave was closed, and hydrogen was passed in from a cylinder. Heating was at 180° for 4-5 hours. When, after the autoclave had cooled, it was found that the pressure differed greatly from its initial value, a fresh portion of hydrogen was passed in and hydrogenation was continued. When hydrogenation was complete, the autoclave was cooled, the solution of the hydrogenation product was filtered, cyclohexane was distilled from the filtrate, and the residue was heated at 300° at a residual pressure of 4-5 mm for 15-20 minutes. The molecular weights of the polyalkylenearyls and polyalkylenecycloalkys were determined viscosimetrically. The results are given in Table 1.

SUMMARY

1. It was found that the hydrogenation of polyalkylenearyls in presence of Raney nickel results in the formation of polyalkylenecycloalkyls – polymers of a new type, the chains of which contain cycloalkane and alkane residues.

2. It was shown that the hydrogenation of polyalkylenearyls is accompanied by a considerable weakening of their color.

3. Suggestions are made concerning the source of the color of polyalkylenearyls and the causes of its weakening as a result of hydrogenation.

LITERATURE CITED

[1] H. Staudinger, E. Geiger, E. Huber, Ber. 62, 263 (1929).

[2] H. Staudinger, V. Wiedersheim, Ber. 62, 2406 (1929).

[3] V.V. Korshak, G.S. Kolesnikov, and A.V. Kharchevnikova, Proc. Acad. Sci. USSR 56, 169, (1947).

[4] G.S. Kolesnikov, V.V. Korshak, and T.V. Smirnova, in the Collection "Chemistry and Physical Chemistry of Macromolecular Compounds", Acad. Sci. USSR Press, Moscow, 1952, p. 44.

[5] Organic Synthesis, Foreign Lit. Press, Moscow, 1952, Collected Vol. 3, p. 338.

---

* Yu. I. Chizhevsky collaborated in the experimental work.

[6] G.S. Kolesnikov, V.V. Korshak, and T.V. Smirnova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1961, No. 5, 898.

Received June 12, 1964

Institute of Heteroorganic Compounds of the USSR Academy
of Sciences

[illegible]

BLANK
PAGE

MACROMOLECULAR COMPOUNDS

COMMUNICATION 84. POLYCONDENSATION OF 1,2-DICHLOROETHANE WITH TOLUENE

G.S. Kolesnikov, V.V. Korshak, and T.A. Soboleva

Two of us with Fedorova [1] have shown that, in the condensation of chlorobenzene with 1,2-dichloroethane in presence of aluminum chloride, a much smaller excess of the aromatic compound is necessary for the formation of three-dimensional polymers than in the polycondensation of benzene with 1,2-dichloroethane, so that a single substituent in benzene must hinder the formation of three-dimensional polycondensational products. Continuing this investigation, we have studied the polycondensation of 1,2-dichloroethane with toluene, which, like chlorobenzene, is a monosubstituted benzene. In toluene the substituent is somewhat larger than in chlorobenzene (the radii of the substituents are 1.09 and 0.99 A, respectively) [2]. Also, in alkylations in presence of aluminum chloride, the methyl group, unlike the chlorine atom, directs a second substituent into the meta position.

In our experiments on the polycondensation of 1,2-dichloroethane with toluene in presence of aluminum chloride, the concentration of catalyst, the temperature and the duration of the reaction were kept constant. The toluene : dichloroethane ratio was varied, but the amount of toluene was kept constant. The catalyst concentration was 3 mole-% on the toluene. The experimental procedure was the same as that used for the experiments with benzene [3] and chlorobenzene [1]. When separating reaction products of low molecular weight by vacuum distillation we collected a fraction boiling up to 200° (3 mm), which consisted essentially of ar,ar'-dimethylbibenzyl, and a fraction boiling at 200-250° (3 mm), consisting mainly of bis(2-tolylethyl)-toluene. The residue of poly[ethylenetolyl] was not treated further. The formation of these products can be represented by the scheme:

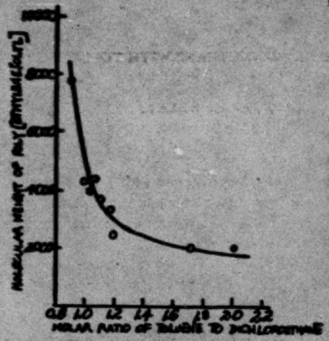
$$2C_6H_5CH_3 + ClCH_2CH_2Cl \xrightarrow{AlCl_3} CH_3C_6H_4CH_2CH_2C_6H_4CH_3 + 2HCl;$$

$$CH_3C_6H_4CH_2CH_2C_6H_4CH_3 + ClCH_2CH_2Cl + C_6H_5CH_3 \xrightarrow{AlCl_3}$$
$$\rightarrow CH_3C_6H_4CH_2CH_2C_6H_3(CH_3)CH_2CH_2C_6H_4CH_3;$$

$$(n+1)C_6H_5CH_3 + nClCH_2CH_2Cl \xrightarrow{AlCl_3} CH_3C_6H_4[CH_2CH_2C_6H_3(CH_3)]nH + 2nHCl.$$

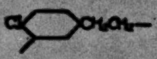
The results of the experiments on the polycondensation of 1,2-dichloroethane with toluene are shown in the table and figure.

It will be seen from the table and figure that the molecular weight of the polycondensation product increases as the excess of toluene diminishes and attains a maximum when there is a small excess of dichloroethane. No three-dimensional polycondensation products are formed when there is an excess of toluene and even when the reactants are taken in equimolecular proportions; a three-dimensional product is formed only when the dichloroethane is in excess. A comparison of the conditions required for the formation of three-dimensional polymer in the polycondensations of toluene and benzene [3, 4] shows that, under given conditions (catalyst concentration, duration and temperature of the reaction), the formation of such a polymer is more difficult in the case of toluene. This may be the result of steric hindrance in that the benzene nuclei in poly[ethylenetolyl] contain three substituents, whereas in poly[ethylenephenyl] they contain only two. It is interesting to note that the formation of three-dimensional polymers from toluene is even more difficult than their formation from chlorobenzene, although both compounds are monosubstituted benzenes and their potential functionalities are identical. The cause of this may lie both in the size of the substituent and in the relative positions of the three substituents in the repeating unit of the polycondensation product. It is unlikely that the sizes of the substituents can be the main cause of the less ready formation of three-dimensional polymer by toluene, since the methyl group is only slightly larger than the chlorine atom. The main cause of this behavior must probably be sought in the structure of poly[ethylenetolyl].



Dependence of the molecular weight of poly[ethylenetolyl] on the relative amounts of reactants.

In poly[chloro(ethylene)phenyl] the repeating unit has the structure:



and a fourth substituent may enter the nucleus (as it must do for the formation of ramified and three-dimensional polycondensation products) in the ortho position with respect to the chlorine atom. The entry of a fourth substituent in this position is facilitated by the ortho-directing power of the chlorine atom and by the tendency of the aliphatic $-CH_2CH_2-$ bridge to direct substituents to the meta position, i.e. the ortho position with respect to the chlorine. It is probable that the structure of poly[ethylenetolyl] differs from that of poly[chloro(ethylene)phenyl].

In order to determine the structure of the polycondensation products obtained from 1,2-dichloroethane and toluene, we carried out the destructive oxidation of ar,ar'-dimethylbibenzyl, bis(2-tolylethyl)toluene, and poly[ethylenetolyl] with dilute nitric acid under pressure. Before being oxidized, dimethylbibenzyl was redistilled, and the fraction boiling at 139-140° (6 mm) was collected. The oxidation of ar,ar'-dimethylbibenzyl yielded isophthalic and terephthalic acids, identified by the melting points of their dimethyl esters, the values obtained being 64-66° for the isophthalic ester (the literature [5] gives 66-67°) and 137-139° for the terephthalic ester (the literature [6] gives 140°). Values obtained for the equivalent weight of isophthalic acid were 81.2 and 82.3 (calculated value: 83.06). The dimethyl terephthalate that we obtained showed no melting point depression in admixture with pure authentic dimethyl terephthalate. The ar, ar'-dimethylbibenzyl was therefore probably a mixture of the 3,3' and 4,4' isomers, though the possibility of the presence of 3,4'-dimethylbibenzyl in the mixture cannot be excluded – the formation of this compound was postulated by Friedel and Crafts for the reaction of toluene with 1,2-dibromoethane [7]. The analytical results for the dimethylbibenzyl were in close accord with the calculated values.

Found %: C 91.38; 91.15; H 8.69; 8.58
$C_{16}H_{18}$: Calculated %: C 91.37 H 8.63

Before being oxidized, bis(2-tolylethyl)toluene was redistilled, and the fraction boiling at 230-245° (3 mm) was collected. The analytical results for this fraction were in close accord with the calculated values.

Found %: C 91.07; 91.11; H 8.84; 8.78
$C_{23}H_{26}$. Calculated %: C 91.41; H 8.59

The oxidization of bis(2-tolylethyl) toluene and poly[ethylenetolyl] with dilute nitric acid at 220° under pressure resulted in the isolation of a mixture of isophthalic and terephthalic acids; no benzenetricarboxylic acid could be isolated. This could be explained both by decarboxylation of any benzenetricarboxylic acid formed under the conditions of the reaction, and also by oxidation of the benzenetricarboxylic acid with rupture of the aromatic ring. When the poly[ethylenetolyl] was oxidized with dilute nitric acid (sp. gr. 1.1) at 180° under pressure, some trimesic acid was obtained, in addition to isophthalic and terephthalic acids. The trimesic acid was identified as its trimethyl ester, which melted at 141-142° (the literature [8] gives 144°). The ester obtained showed a considerable depression in melting point when mixed with dimethyl terephthalate. The analytical results for the trimethyl trimesate were in close accord with the calculated values.

Found %: C 57.35; 57.59; H 4.68; 4.80

$C_{12}H_{12}O_6$. Calculated %: C 57.14; H 4.80

TABLE

Polycondensation of 1,2-Dichloroethane with Toluene

Molar ratio of toluene to dichloroethane	Yield (%)			Specific viscosity of a 3% solution of poly[ethylenetolyl] in benzene	Molecular weight of poly[ethylenetolyl]
	ar,ar'-Dimethylbibenzyl	Bis(2-tolylethyl) toluene	Poly[ethylenetolyl]		
2.02	20.4	17.7	24.7	0.090	1970
1.71	14.1	11.9	55.2	0.091	1990
1.18	3.4	6.3	50.3	0.112	2440
1.16	3.1	3.7	47.6	0.152	3320
1.10	2.8	2.2	48.2	0.163	3570
1.06	3.3	3.7	45.8	0.205	4480
1.025	3.5	6.3	44.1	0.180	3940
1.00	3.8	4.6	41.1	0.196	4280
0.985	4.5*	3.9*	43.2**	0.360***	7870***

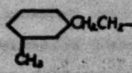
---

* On toluene taken.

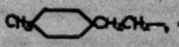
** On toluene taken; it consists of 29.1% soluble product and 14.1% insoluble product.

*** Of soluble product.

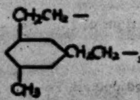
The formation of trimesic, isophthalic, and terephthalic acids in the oxidation of poly[ethylenetolyl] indicates that this polymer contains structural units in which the aliphatic substituents are oriented meta or para to one another. Such units could be:



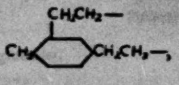
(I)



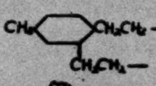
(II)



(III)



(IV)



(V)

(I) and (II) can exist only as terminal groups, and their oxidation will result in the formation of isophthalic and terephthalic acids. The oxidation of (III) will give trimesic acid, but subsequent decarboxylation can then yield isophthalic acid. Oxidation of (IV) and (V) should give trimellitic acid, which however, we were unable to isolate; if it is formed at all, it is formed only in very small amount. The proportions of (IV) and (V) in the poly[ethylenetolyl] chain are probably small, but it is quite possible that they are present, since they are formed by reaction of p-ethyltoluene with 1,2-dichloroethane and toluene. It is probable that the main type of repeating unit is (III), so that poly[ethylenetolyl] differs in structure from poly[chloro(ethylene)phenyl]. In poly[ethylenetolyl] the hydrogen atoms available for replacement under the action of dichloroethane in presence of aluminum chloride are screened by neighboring alkyl groups; the orienting influence of the alkyl groups is also unfavorable to the further reaction of poly(ethylenetolyl] with dichloroethane, and only when there is excess of dichloroethane in the reaction mixture does the formation of ramified and three-dimensional polycondensation products become possible. Hence, the cause of the greater difficulty in the formation of a three-dimensional polymer in the polycondensation of dichloroethane with toluene in presence of aluminum chloride lies in the fact that in poly(ethylenetolyl] the substituents are predominantly arranged meta to one another, and this arrangement sterically hinders further substitution.

SUMMARY

1. A study was made of the polycondensation of 1,2-dichloroethane with toluene with formation of poly(ethylenetolyl]. The low-molecular-weight products of this reaction were ar,ar'-dimethylbibenzyl and bis(2-tolylethyl) toluene.

2. The structure of the polycondensation products formed from 1,2-dichloroethane and toluene was established.

3. It was shown that the cause of the greater difficulty with which three-dimensional polymers are formed in the polycondensation of 1,2-dichloroethane with toluene — as compared with the analogous reaction between 1,2-dichloroethane and chlorobenzene — is the steric hindrance that arises from an arrangement of substituents oriented predominantly meta to one another.

LITERATURE CITED

[1] G.S. Kolesnikov, V.V. Korshak, and L.S. Fedorova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 2 359.(T.p. 321)*

[2] Ya. K. Syrkin and M.E. Dyatkina, The Chemical Bond and the Structure of Molecules, State Tech. Press, Moscow, 1946, p. 228.

[3] G.S. Kolesnikov, V.V. Korshak, and T.V. Smirnova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1951, No. 5, 596.

[4] V.V. Korshak, G.S. Kolesnikov and A.V. Kharchevnikova, Proc. Acad. Sci. USSR, 56, 169 (1947).

[5] O. Stark, O. Garben, Ber. 46, 663 (1913).

[6] W.J. Hickinbottom, Reactions of Organic Compounds, United Sci. Tech. Press, 1939, p. 280.

[7] C. Friedel and J.M. Crafts, Bull. Soc. chim. 35, 52 (1881).

[8] Dictionary of Organic Compounds, Foreign Lit. Press, Moscow, 1949, Vol. 3, p. 847.

Received June 30, 1954

Institute of Heteroorganic Compounds of the USSR Academy of Sciences

---

* T.p. = C.B. Translation pagination.

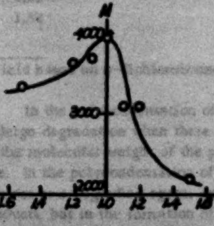
MACROMOLECULAR COMPOUNDS

COMMUNICATION 85. POLYCONDENSATION OF 1, 2-DICHLOROETHANE WITH o-DICHLOROBENZENE

G.S. Kolesnikov and V.V. Korshak*

In studies of the polycondensation of 1, 2-dichloroethane with monosubstituted benzenes (chlorobenzene and toluene), we have already shown that the introduction of even a single substituent into the benzene nucleus greatly hinders the formation of ramified and three-dimensional polycondensation products [1, 2]. It may therefore be supposed that, with the introduction of two substituents into the benzene nucleus, the formation of ramified and three-dimensional polymers will be rendered still more difficult or may even become impossible.

We have made a study of the polycondensation of 1, 2-dichloroethane with o-dichlorobenzene in presence of aluminum chloride with the object of determining the effect of the positions of the substituents in a disubstituted benzene on the course of its polycondensation with 1, 2-dichloroethane. In order to determine the effect of the relative amounts of the reactants, we carried out a series of experiments in which the amounts of o-dichlorobenzene and aluminum chloride and the duration and temperature of the reaction were kept constant, while the amount of dichloroethane was varied over a wide range. Experiments were carried out both with an excess of dichlorobenzene and also with an excess of dichloroethane. In all experiments the catalyst concentration was 6.0 mole-% on the amount of o-dichlorobenzene. The experimental procedure was as in previous investigations [1-3]. In distilling off reaction products of low molecular weight under reduced pressure, we collected a fraction boiling up to 230° (5-6 mm), which we took to be a tetrachlorobibenzyl. The polycondensation product poly[dichloro(ethylene)phenyl] was purified by reprecipitation from a 4% benzene solution by addition of six times the volume of methanol. The molecular weight of the poly[dichloro(ethylene)phenyl] was determined viscosimetrically. The experimental results are given in the figure and in Table 1.



M is the molecular weight of poly[dichloro-(ethylene)phenyl], and is plotted against molar ratio of dichloroethane to dichlorobenzene (on the left) and molar ratio of dichlorobenzene to dichloroethane (on the right).

It will be seen from Table 1 and the figure that the polycondensation of 1, 2-dichloroethane with o-dichlorobenzene takes place, irrespective of which of the reactants is in excess, and no insoluble, three-dimensional polymers are formed, even when there is a considerable excess of dichloroethane. Hence, introduction of two substituents into the benzene nucleus of the aromatic reactant affects the reaction in such a way that, at low catalyst concentrations (up to 6 mole-%), of the four hydrogen of o-dichlorobenzene, only two can be replaced, the potentially quadrifunctional o-dichlorobenzene behaving, therefore, as a bifunctional compound. As the polycondensation of 1, 2-dichloroethane with o-dichlorobenzene must be regarded as a polycondensation reaction between two bifunctional compounds at this particular catalyst concentration then– in accordance with the theory of linear polycondensation [4]– the products of highest molecular weight should be obtained when equimolecular proportions of reactants are used. It will be seen from Table 1 and the figure that products of maximum molecular weight are indeed formed at a molar ratio of o-dichlorobenzene to 1, 2-dichloroethane of 1.0. The yield of macromolecular products is also a maximum at this molar ratio.

The macromolecular polycondensation products obtained from 1, 2-dichloroethane and o-dichlorobenzene are solids. Purification of poly[dichloro(ethylene)phenyl] by reprecipitation resulted only in an insignificant rise in molecular weight, which was the most pronounced in the products having the highest molecular weight. The curve given in the figure for the dependence of the molecular weight of poly[dichloro(ethylene)phenyl] on the relative amounts of reactants, unlike those found, for example, for the polycondensation of dicarboxylic acids with diamines [5] is not symmetrical. We have not found the causes of this behavior, but we can suggest the following possible explanations. We have shown that reaction of dichloroethane with poly[ethylenephenyl] in presence of aluminum chloride results in the formation of insoluble, three-dimensional products, whereas reaction of dichloroethane with poly[dichloro(ethylene)phenyl] has no effect on the molecular weight of the latter at low catalyst concentration (when the catalyst concentration is high, the formation of three-dimensional products is again found). Hence, dichloroethane is not a degrading agent for poly[dichloro(ethylene)phenyl]. On the other hand, the aromatic component of the reaction mixture will degrade the macromolecular polycondensation products.

---

* Z. Kraineva assisted in the experimental work.

TABLE 1.

Polycondensation of 1, 2-dichloroethane with o-dichlorobenzene

Molar ratio	Yield (%)		Molecular weight of poly[dichloro-(ethylene)phenyl]	
	sym-ar-Tetrachlorobibenzyl	Poly[dichloro-(ethylene)phenyl]	Not reprecipitated	Reprecipitated
o-Dichlorobenzene: dichloroethane				
1.50	8.6	59.0	2200	2190
1.20	4.9	66.0	3060	3100
1.10	4.0	60.1	3150	3110
1.00	3.5	68.3	3500	3920
Dichloroethane: o-dichlorobenzene				
1.11	6.0*	40.2*	3550	3720
1.22	5.3*	37.4*	3420	3640
1.52	8.7*	38.8*	3200	3340

---

* Yield based on o-dichlorobenzene

In the polycondensation of dicarboxylic acids with diamines or glycols, the polycondensation products undergo degradation when there is an excess of either reactant and, as a result, the curve for the dependence of the molecular weight of the polycondensation product on the relative amounts of reactants is a symmetrical one. In the polycondensation of 1, 2-dichloroethane with aromatic compounds, only the aromatic reactant can act as a degrading agent: excess of dichloroethane results not in the degradation of the macromolecular products, but in the formation of ramified and three-dimensional products— or it may have no effect at all. This may be one of the causes of the unsymmetrical form of the curve given in the figure. The lowering of the molecular weight when there is an excess of dichloroethane is probably due to the reduction in catalyst concentration brought about by the addition of a large amount of diluent (dichloroethane).

Another possible cause of the asymmetry of the curve is the occurrence of side reactions. A side reaction that may occur when there is an excess of dichloroethane is the conversion of this substance into benzene in presence of aluminum chloride and the formation of polycondensation products by reaction of the benzene with unchanged dichloroethane. Shishido and Yoshikawa [6] found that treatment of 1, 2-dichloroethane with aluminum chloride yielded benzene and m-diphenethylbenzene. We repeated Shishido and Yoshikawa's experiments and found that at 49° with a molar ratio of dichloroethane to aluminum chloride of 6.75: 1, hydrogen chloride was evolved and the reaction mixture became dark brown. The reaction mixture was treated with dilute hydrochloric acid, washed with water, and dried with calcium chloride. Unchanged dichloroethane was distilled off, and vacuum distillation then yielded a very small amount of a high-boiling substance of indefinite boiling point. The residue was a dark-colored substance, and it was found to be poly[ethylenephenyl] of molecular weight 2510. The yield of poly[ethylenephenyl] was 19.2%, calculated on the amount of dichloroethane taken, it being assumed that the reaction proceeded as follows:

$$(4n + 3)ClCH_2CH_2Cl \xrightarrow{AlCl_3} H(C_6H_4CH_2CH_2)_nC_6H_5 + (8n + 6)HCl.$$

For convenience of calculation we assume that four molecules of dichloroethane give one repeating unit of poly[ethylenephenyl]. The poly[ethylenephenyl] was identified by oxidation at the boil with chromic acid mixture to yield terephthalic acid, identified as its methyl ester, m.p. 139-140°, undepressed by admixture with pure authentic dimethyl terephthalate.

The first stage of the reaction is probably the formation of benzene:

$$3ClCH_2CH_2Cl \xrightarrow{AlCl_3} C_6H_6 + 6HCl,$$

which then reacts with dichloroethane with formation of poly[ethylenephenyl]:

$$(n + 1)C_6H_6 + nClCH_2CH_2Cl \xrightarrow{AlCl_3} C_6H_5(CH_2CH_2C_6H_4)_nH + 2nHCl.$$

Thus, when the dichloroethane is in excess, not only the main polycondensation reaction will occur with formation of poly[dichloro(ethylene)phenyl], but also, possibly, a reaction leading to the formation of poly[ethylenephenyl]. This side reaction can also distort the course of the curve shown in the figure. Naturally, when the aromatic reactant is in excess, this reaction does not occur, or occurs only to a very slight extent.

When the catalyst concentration is increased to 12.0 mole-% (on the amount of o-dichlorobenzene), the character of the dependence of the molecular weight of poly[dichloro(ethylene)phenyl] on the relative amounts of the reactants is unaffected, and the molecular weight rises as the proportions approach equimolecular values. The results for the polycondensation of dichloroethane with o-dichlorobenzene in presence of 12.0 mole-% of aluminum chloride are given in Table 2.

TABLE 2

Polycondensation of 1, 2-Dichloroethane with o-Dichlorobenzene

Molar ratio of o-dichlorobenzene to dichloroethane	Yield (%)		Molecular weight of poly[dichloro-(ethylene)phenyl]	
	sym-ar-Tetrachlorobibenzyl	Poly[dichloro-(ethylene)phenyl]	Not reprecipitated	Reprecipitated
1.20	5.2	71.3	2690	3360
1.10	3.6	68.0	3510	4070
1.00	1.9	66.3	3510	5590

In order to determine the effect of catalyst concentration on the course of the polycondensation of dichloroethane with o-dichlorobenzene, two series of experiments were carried out. In each series all of the experimental conditions were constant with the exception of the catalyst concentration, which was varied. One series was carried out with an excess of o-dichlorobenzene, and the other with an excess of dichloroethane. The results are given in Tables 3 and 4.

Table 3 shows that, when o-dichlorobenzene is in excess and the catalyst concentration is low, the polycondensation reaction does not occur. When the catalyst concentration is increased, polycondensation occurs with formation of poly[dichloro(ethylene)phenyl], the molecular weight of which rises with increase in catalyst concentration.

The effect of catalyst concentration is somewhat different when the 1, 2-dichloroethane is in excess, as can be seen from Table 4. At low catalyst concentration polycondensation does not go readily and the yield of poly[dichloro(ethylene)phenyl] is low. Increase in catalyst concentration results in increase in the yield of poly[dichloro(ethylene)phenyl] and an increase also in its molecular weight. When a certain concentration of catalyst is attained the formation of soluble polycondensation products is accompanied by the formation of an appreciable amount of infusible, insoluble, three-dimensional polymers. It is interesting to note that the formation of insoluble three-dimensional polymers is accompanied by a fall in the molecular weight of the soluble polymeric product. The explanation of this may be that the cross-linking reaction occurs in the first place at the expense of the longer molecules, as shown previously by the present authors in collaboration with Soboleva [7]. The formation of three-dimensional polymers is accompanied also by a reduction in the yield of sym-ar-tetrachlorobibenzyl.

TABLE 3

Polycondensation of 1,2-Dichloroethane with o-Dichlorobenzene

Catalyst concentration in mole-%			Yield (%)		Molecular weight of poly[dichloro-(ethylene)phenyl]	
on dichlorobenzene	on dichloroethane	on dichloroethane + dichlorobenzene	sym-ar-Tetrachlorobibenzyl	Poly[dichloro-(ethylene)phenyl]	Not reprecipitated	Reprecipitated
1.50	1.80	0.82	2.2	–	–	–
3.00	3.60	1.63	2.9	32.8	2690	2740
6.00	7.20	3.27	4.9	66.0	3060	3100
12.00	14.40	6.55	5.2	71.3	2890	3360

TABLE 4

Polycondensation of 1, 2-Dichloroethane with o-Dichlorobenzene (molar ratio of dichloroethane to dichlorobenzene = 1.52)

Catalyst concentration in mole-%			Yield (%)*		Molecular weight of poly[dichloro-(ethylene)phenyl]	
on dichlorobenzene	on dichloroethane	on dichloroethane + dichlorobenzene	sym-ar-Tetrachlorobibenzyl	Poly[dichloro-(ethylene)phenyl]	Not reprecipitated	Reprecipitated
3.00	1.97	1.19	3.7	11.7	3010	3150
6.00	3.94	2.38	8.7	38.6	3200	3340
7.50	4.93	2.97	7.2	49.4	4250	4830
12.00	7.89	4.76	4.5	92.7**	2930***	3370***

---

* Yields calculated on amount of o-dichlorobenzene taken.

** Including 74.1% of three-dimensional polymer and 16.6% of soluble polymer

*** Of the soluble product

The polycondensation of 1, 2-dichloroethane with o-dichlorobenzene in presence of aluminum chloride can be represented as follows:

$$(n+1)C_6H_4Cl_2 + nClCH_2CH_2Cl \xrightarrow{AlCl_3}$$

$$\longrightarrow H(Cl_2C_6H_2CH_2CH_2)_nC_6H_3Cl_2 + 2nHCl.$$

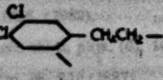
The repeating unit of the polycondensation product should have the composition $C_6H_2Cl_2CH_2CH_2$, corresponding to a chlorine content of 40.98%. Chlorine determinations on the macromolecular polycondensation product obtained gave values of 36.25% and 37.08% (average values). The difference between the experimentally found and calculated chlorine contents is outside the limits of experimental error. The low chlorine content was associated with high carbon and hydrogen contents, the experimentally determined values being 59.22, 58.59% and 4.36, 4.89%, respectively, and the corresponding calculated values 55.52% and 3.50%.

We consider that the observed departure of the composition of the polycondensation products from the calculated value may be explained by the transfer of chlorine atoms from one aromatic compound or polycondensation product to another in presence of aluminum chloride. Halogen-transfer reactions of this sort have been described in the literature. Thus, Dumreicher [8] observed the formation of dibromobenzene and benzene when bromobenzene was heated with aluminum chloride. Friedel and Crafts [9] observed chlorine transfer in the methylation of o-dichlorobenzene in presence of aluminum chloride; the main reaction products were hexamethylbenzene and trichloromesitylene. Treatment of p-dibromobenzene with aluminum chloride gave a mixture of bromobenzene, m- and p-dibromobenzenes, and two tribromobenzene isomers [10]. Roux [11] observed the formation of naphthalene, 2-bromonaphthalene, and dibromnaphthalenes when 1-bromonaphthalene was heated with aluminum chloride. Halogen transfer in presence of aluminum chloride has been observed in many other substances [12-14].

It is therefore quite probable that the polycondensation process may be accompanied by halogen redistribution with the result that the chlorine content of the polycondensation product formed from 1, 2-dichloroethane and o-dichlorobenzene will be reduced. The resulting polychlorobenzene is apparently distilled off with the ar-tetrachlorobibenzyl during the vacuum distillation.

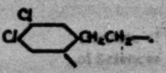
With the object of determining the structure of the polycondensation product formed from 1, 2-dichloroethane and o-dichlorobenzene, we carried out its destructive oxidation. Attempts to oxidize it with boiling chromic acid mixture and with boiling dilute nitric acid at atmospheric pressure were unsuccessful. We succeeded in oxidizing it with dilute nitric acid (sp.gr. 1.1) at 220-250° and at 65-80 atm pressure. As a result of the oxidation an acid melting at 196-198° was obtained. Its equivalent weight was determined (duplicate results: 116.5 and 119.0), and the values obtained indicated that it was one of the dichlorobenzenedicarboxylic acids (calculated equivalent weight: 117.5). Values of 30.34 and 30.48% were found for the chlorine content, which are in close accord with the value calculated for a dichlorobenzenedicarboxylic acid (30.18%). The melting point of the acid corresponds to that of 4, 5-dichlorophthalic acid, which melts at about 200° [15].

On the basis of the structure of the oxidation product, it may be deduced that the polycondensation product formed from 1, 2-dichloroethane and o-dichlorobenzene consists mainly of repeating units of the following structure:



and it may be called poly[4, 5-dichloro-2-ethylenephenyl]. Such a structure is in accord with the orienting effects of the substituents: each aliphatic residue is in the para position to a chlorine atom.

From the distillate obtained in the vacuum distillation – which we had assumed to be a symmetrical ar-tetrachlorobibenzyl – we isolated a substance which, after recrystallization from methanol, melted at 97-98°. Values found for its chlorine content were 44.81 and 44.93%, and the chlorine content calculated for $C_{14}H_{10}Cl_4$ is 44.32%. No symmetrical ar-tetrachlorobibenzyls have been described in the literature, but our product appeared to be 3, 4, 3', 4'-tetrachlorobibenzyl, for only this isomer, reacting with dichloroethane and o-dichlorobenzene, could give a polymer having the repeating unit



The assumed structure of the tetrachlorobibenzyl was confirmed by the results of the oxidation of the compound. The product obtained by oxidizing it with chromic anhydride in glacial acetic acid contained chlorine, was soluble in alkali, and melted at 195-196°. The literature gives a melting point of 203° for 3, 4-dichlorobenzoic acid [16] and 166° for 2, 3-dichlorobenzoic acid [17]. Values obtained for the chlorine content were 36.31 and 36.44%, and the calculated value for $C_7H_4O_2Cl_2$ is 37.13%.

SUMMARY

1. A study was made of the polycondensation of 1, 2-dichloroethane with o-dichlorobenzene, and the principal laws governing the process were established.

2. It was found that, when the catalyst concentration is low, o-dichlorobenzene behaves as a bifunctional compound, in spite of the fact that its potential functionality is four.

3. The structure of the polycondensation products formed from 1, 2-dichloroethane and o-dichlorobenzene was determined.

4. It was found that treatment of 1, 2-dichloroethane with aluminum chloride resulted in the formation of poly[ethylenephenyl].

LITERATURE CITED

[1] G.S. Kolesnikov, V.V. Korshak, and L.S. Fedorova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 2, 353 (T.p. 321)*

[2] G.S. Kolesnikov, V.V. Korshak, and T.A. Soboleva, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 6, 1095 (T.p. 1007)*

[3] G.S. Kolesnikov, V.V. Korshak, and T.V. Smirnova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1951, 596.

[4] V.V. Korshak, Chemistry of Macromolecular Compounds, Acad. Sci. USSR Press, 1950.

[5] V.V. Korshak, V.V. Golubev, and G.S. Kolesnikov, Investigations on Macromolecular Compounds, Acad. Sci. USSR Press, Moscow and Leningrad, 1949, p. 22.

[6] K. Shishido, Y. Yoshikawa, J. Am. Chem. Soc., 70, 1608 (1948).

[7] V.V. Korshak, G.S. Kolesnikov, and T.A. Soboleva, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 365 (T.p. 327)*

[8] O. Dumreicher, Ber., 15, 1866, (1882).

[9] C. Friedel, J.M. Crafts, Ann. chim. phys. (6), 10, 411 (1887).

[10] A.J. Lerey, Bull. soc. chim. 48, 210 (1887).

[11] L. Roux, Bull. soc. chim. 45, 510 (1886).

[12] M. Copisarow, C.H.N. Long, J. Chem. Soc. 119, 442 (1921).

[13] M. Kohn, F. Bum, Monatsch., 33, 923 (1912).

[14] M. Kohn, A. Pink, Monatsch., 44, 1813 (1923).

[15] V. Villiger, Ber. 42, 3529 (1909).

[16] F.F. Beilstein and A. Kuhlberg, Ann. 152, 224 (1869).

[17] E. Hope, G.S. Riley, J. Chem. Soc. 123, 2478 (1923).

Received June 30, 1954

Institute of Heteroorganic Compounds of the USSR Academy of Sciences

---

* T.p. = C.B. Translation pagination.

MACROMOLECULAR COMPOUNDS

COMMUNICATION 86. DETERMINATION OF THE MOLECULAR WEIGHTS OF POLYAMIDES FROM THE VISCOSITIES OF THEIR SOLUTIONS IN CRESOL AND IN METHANOL

V.V. Korshak and S.A. Pavlova

The molecular weights of polymers can be determined rapidly and accurately by the viscosity method so long as the method has been satisfactorily calibrated against some other method of determining molecular weights. There is no theory in existence that would directly relate the results of viscosity measurements on polymers with the molecular weights of the polymers. Staudinger's formula $[\eta] = kM$ [1], as later experimental investigations have shown, is not always valid, being only a special case of some more general law. It is therefore necessary to turn to absolute methods of measurement, such as osmometry, cryoscopy, sedimentation in the ultracentrifuge, light scattering, etc.

We were faced with the problem of determining the empirical relationship between the molecular weights of polyamides and the viscosities of their dilute solutions. The available data on this matter derive from the investigations of Staudinger [2], who studied this relationship for solutions of a polyamide in cresol. The molecular weight of the original polyamide was determined by the osmotic pressure method. On the basis of his results, Staudinger proposed the formula $Z_\eta = 1.2 \cdot 10^{-4} n$, relating the viscosity number Z_η with the number n of repeating units in the polymer chain. All measurements were done at finite concentrations without extrapolation to infinite dilution. The molecular weights of the polymers studied by Staudinger were in the range 6600-8600. This formula is widely used, even at the present time. Its defects include, first, the derivation of the formula for molecular weights which are in the low region and cover too short a range and second, its derivation on the basis of data obtained at a finite concentration. Since these investigations of Staudinger were published, many further studies have been made of the viscosities of dilute solutions of polymers and their dependence on the molecular weights of the polymers [3-7].

It was found that this relationship cannot be expressed by the simple Staudinger formula for a wide range of molecular weights and is expressed more satisfactorily by $[\eta] = KM^a$ K and a being empirical constants [8]. Experiment showed that a varies among various polymer-solvent systems from 0.5 to 1.5. Many attempts have been made to elucidate the physical significance of this formula. These theoretical investigations amount to the use of various model concepts to establish the relationship between the volume occupied by the macromolecule and its hydrodynamic interaction with a stream of solvent, as affected by the degree of convolution of the macromolecule [6,7]. It was found that, for a highly convoluted polymeric chain, such that the stream of solvent cannot penetrate it but can only flow around its surface, a will be 0.5 (i.e. the viscosity of the solution will be proportional to the square root of the molecular weight of the dissolved polymer). As the structure of the convoluted ball formed by the macromolecule becomes more open and becomes more penetrable by solvent, a increases, attaining the value of unity when the macromolecule is fully accessible, so that the formula $[\eta] = KM^a$ is transformed into Staudinger's formula. The fact that values of a greater than unity are found experimentally has not yet been explained. The study of viscosity can, to a certain extent, give an idea of the form of the macromolecule in the solution and its size.

Staudinger, and also other authors, proposed another formula, which was found to be valid over a wider range of molecular weights. The physical significance of this formula $[\eta] = KM + J$ has not been elucidated. This formula has two empirical constants, K and J [9].

Our object in this investigation was to determine the relationship of viscosities of solutions of a polymer in cresol and in methanol to the molecular weight of the polymer. We considered that it was essential to extend the range of molecular weights for which the empirically determined relationship would be valid. As indicated above, Staudinger's formula was derived for polymers having molecular weights of not above 8600, whereas the polyamides that have attracted the greatest practical interest and have been most extensively used have higher molecular weights in the range 15,000-25,000. It was of interest also to compare the two formulas cited above in order to determine which of them gives the better representation of the relationship found.

EXPERIMENTAL

The polymers taken for investigation were fractions derived from some samples of mixed polyamide, the preparation and fractionation of which have been described previously [10]. The molecular weights of these fractions were determined by a method based on measurements of sedimentation in the ultracentrifuge and of diffusion, which has also been described in previous papers [10].

Viscosity Measurements

The viscosities of solutions of the polyamide were determined in cresol and in methanol at various concentrations. The measurements were made in an Ostwald viscometer at 20 ± 0.005°. The solvents cresol and methanol – were not subjected to any special purification process. Tables 1 and 2 give the results of the measurements and give also reduced viscosities (η/c) extrapolated to infinite dilution by the method of least squares. Table 3 gives the results of viscosity measurements in methanol at a concentration of 5 g/liter.

TABLE 1

Viscosities of Polyamide Fractions in Cresol

M 46,600		M 21,700		M 17,600		M 27,500		M 58,500	
c g/liter	η/c	c g/liter	η/c	c g/liter	η/c	c g/liter	η/c	c g/liter	η/c
2.28	0.385	5	0.160	5	0.100	5	0.235	5	0.540
1.82	0.378	5	0.163	5	0.100	5	0.241	5	0.510
1.36	0.385	4	0.169	4	0.097	4	0.230	4	0.485
0.91	0.378	4	0.158	4	0.099	4	0.231	4	0.485
0.46	0.351	3	0.157	3	0.095	3	0.216	3	0.460
$[\eta] = 0.375$		3	0.150	3	0.096	3	0.216	3	0.462
		2	0.160	2	0.090	2	0.220	2	0.465
		2	0.144	2	0.088	2	0.205	2	0.465
		1	0.150	1	0.082	1	0.221	1	0.466
		1	0.139	1	0.080	1	0.219	1	0.451
		$[\eta] = 0.142$		$[\eta] = 0.0820$		$[\eta] = 0.179$		$[\eta] = 0.425$	

Discussion of Results

Our results show that for cresol and methanol solutions of polyamides it is not possible to find a general relationship between viscosity and concentration of the form proposed by other authors [11]:

$$\eta/c = [\eta] + k[\eta]^2 c.$$

It was, however, found to be possible to obtain an expression for the relationship between the viscosities of cresol and methanol solutions of polyamides and the molecular weights on the basis of our experimental results. The relationship that we have obtained between the intrinsic viscosity of the polyamide in cresol and its molecular weight can be expressed as follows: $[\eta] = 0.29 \cdot 10^{-6} \cdot M^{1.3}$ or $[\eta] = 8.58 \cdot 10^{-6} \cdot M - 0.0551$. For the first formula the sum of the squares of discrepancies in the experimental values is $\Sigma\Delta^2 = 0.03162$, whereas for the second it is $\Sigma\Delta^2 = 0.001848$, so that the second formula would appear to be more accurate than the first. The same is true of the results obtained at 5 g/liter.

We considered it to be desirable to find the relationship between the viscosity of the polyamide solution and the molecular weight, not only for values extrapolated to infinite dilution, but also for values obtained at a concentration of 5 g/liter. Such a relationship will make it possible to obtain the necessary data for the determination of the molecular weight from two parallel measurements without the determination of the dependence of viscosity on concentration for each sample, which is a rather arduous task.

$(\eta/c)_{c=5} = 0.522 \cdot 10^{-6} M^{1.38}$ or $(\eta/c)_{c=5} = 9.5 \cdot 10^{-6} M - 0.0468$; $\Sigma\Delta^2 = 0.001978$; $\Sigma\Delta^2 = 0.00089$.

However, plotting of Staudinger's results for the viscosity of a polyamide in cresol in Figures 1 and 2 showed that for the first variant these points lie very satisfactorily between the curves calculated for the $c =$ and $c = 5$ g/liter formulas; for the second variant the discrepancy is too great.

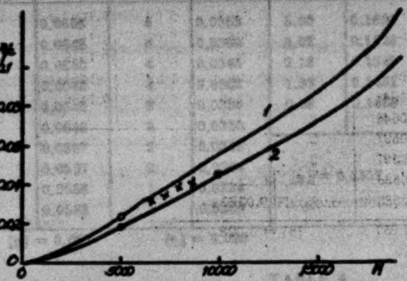


Fig. 1. 1 - curve calculated from the formula $(\eta/c)_{c=5} = 0.25 \cdot 10^{-6} M^{1.38}$; 2 - curve calculated from the formula $[\eta] = 0.29 \cdot 10^{-6} M^{1.30}$; x – Standinger's results

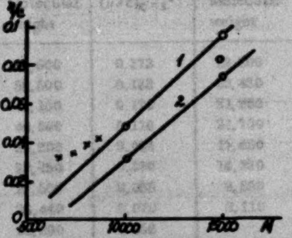


Fig. 2. 1 - curve calculated from the formula $(\eta/c)_{c=5} = 9.5 \cdot 10^{-6} M - 0.0468$; 2 - curve calculated from the formula $[\eta] = 8.6 \cdot 10^{-6} M - 0.055$; x – Staudinger's results

We can consider it to be established, therefore, that for the wide range of molecular weights investigated (6600-58500), the formula in which M is raised to a power is the best expression of the relationship sought.

For methanol solutions, the relationship between viscosity and molecular weight can be expressed by the formulas:

$$[\eta] = 5.2 \cdot 10^{-6} M^{0.9} \text{ and } [\eta] = 1.55 \cdot 10^{-6} M + 0.0084$$

$$(\eta/c)_{c=5} = 3.9 \cdot 10^{-6} M^{0.88} \text{ and } (\eta/c)_{c=5} = 2.10 \cdot 10^{-6} M + 0.011.$$

In this case the two variants are found to be equally accurate, so that either may be used with success over the range of molecular weights studied.

It is interesting to consider the difference in the values of the index a in the two systems. For polyamides in methanol $a = 0.9$. The specific viscosities of solutions in methanol are very much less than those of solutions in cresol. These facts indicate that, in methanol, the polyamide macromolecule has the form of a rather compactly coiled ball, in agreement with our earlier results in an investigation of sedimentation in the ultracentrifuge and diffusion. The power index for the polyamide-cresol system is $a = 1.3$, i.e. it must be supposed that, as a result of powerful solvation by cresol molecules, the macromolecule exists in a highly extended state in the solution.

TABLE 2

Viscosities of Polyamide Fractions in Methanol

M 58,500		M 27,500		M 17,600		M 75,600		M 21,700	
c (g/liter)	η/c	c (g/liter)	η/c	c (g/liter)	η/c	c (g/liter)	η/c	c (g/liter)	η/c
5	0.1291	5	0.0656	5	0.0363	5.00	0.1690	5	0.0562
5	0.1290	5	0.0646	5	0.0360	3.02	0.1536	5	0.0578
4	0.1221	4	0.0650	4	0.0345	2.18	0.1548	4	0.0548
4	0.1191	4	0.0640	4	0.0362	1.39	0.1451	4	0.0573
3	0.1172	3	0.0648	3	0.0350	0.08	0.1460	3	0.0537
3	0.1138	3	0.0648	3	0.0350			3	0.0598
2	0.1089	2	0.0597	2	0.0316			2	0.0503
		2	0.0597	2	0.0304	[η] = 0.1317		2	0.0575
1	0.1030	1	0.0586	1	0.0234			1	0.0492
1	0.1007	1	0.0585	1	0.0360			1	0.0482
[η] = 0.087		[η] = 0.057		[η] = 0.028				[η] = 0.048	

TABLE 3

Viscosities of Polyamide Fractions in Methanol at a Concentration of 5 g/liter

Molecular weight	$(\eta/c)_{c=5}$*	Molecular weight	$(\eta/c)_{c=5}$*
75,600	0.173	22,800	0.048
58,500	0.128	22,430	0.061
42,160	0.125	21,960	0.056
40,060	0.116	21,700	0.058
29,200	0.084	17,600	0.036
28,450	0.070	16,330	0.054
27,500	0.066	8,550	0.015
26,440	0.070	3,110	0.018
23,200	0.056		

TABLE 4

Viscosities of Polyamides in Cresol from Staudinger's Paper [2]

c (g/liter)	Z_η	Molecular weight
4.07	0.0322	6600
3.97	0.0345	7300
3.14	0.0388	8000
2.45	0.0404	8600

---

* $(\eta/c)_{c=5}$ is the reduced viscosity at a concentration of 5 g/liter.

SUMMARY

1. A study was made of the relationship between the viscosities of dilute solutions of polyamides in cresol and the molecular weights of the polyamides. The relationship found can be expressed by the formulas: $[\eta] = 0.29 \cdot 10^{-4} M^{1.3}$ or $[\eta] = 8.58 \cdot 10^{-6} M - 0.055$.

2. A study was made of the relationship between the viscosities of dilute solutions of polyamides in methanol and the molecular weightsof the polyamides. The relationship found can be expressed by the formulas: $[\eta] = 5.2 \cdot 10^{-6} M^{0.9}$ or $[\eta] = 1.55 \cdot 10^{-6} M + 0.0084$.

3. It was found that the formula in which M is raised to a power expresses the relationship between the viscosity of a polymer solution and the molecular weight of the polymer better than the Staudinger formula with a constant term.

LITERATURE CITED

[1] H. Staudinger, Ber. 63, 222, 721 (1930).

[2] H. Staudinger, H. Jörder, Journ. prakt. Chem. 160, 176 (1942).

[3] Ch. Sadron, Journ. Pol. Sci. 3 (1948).

[4] H. Mark, Monatsh. 81, 140 (1950).

[5] P.I. Flory, T.G. Fox, Journ. Am. Chem. Soc. 73, 1904 (1951).

[6] T.G. Kirkwood, J. Risemann, J. Chem. Phys. 16, 565 (1948).

[7] P. Debye, A.M. Bueche, J. Chem. Phys. 16, 573 (1948).

[8] H. Mark, Journ. Am. Chem. Soc. 65, 2319 (1943).

[9] P.I. Flory, Stickney, Journ. Am. Chem. Soc. 62, 3032 (1940).

[10] S.E. Bresler, V.V. Korshak, S.A. Pavlova, and P.A. Finogenov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, No. 2, 344 (T.p. 283)*, 354 (T.p. 291)*.

[11] M. Huggins, Journ. Am. Chem. Soc. 64, 2716 (1942).

Received August 18, 1954

Institute of Heteroorganic Compounds of the USSR Academy of Sciences

---

* T.p. = C.B. Translation pagination.

BLANK
PAGE

POLYCONDENSATION OF GLYCINE ETHYL ESTER

V.V. Korshak, K.T. Poroshin, and T.D. Kozarenko

In a previous paper [1] we have shown that the presence of various acidic substances (organic and inorganic) can greatly affect the polycondensation reactions of esters of DL-alanine. At the same time it was pointed out that the regularities observed in this reaction can be extended also to the esters of other α-amino acids. In this connection, it was of interest to study this process in greater detail for glycine esters, for it is known that in the polycondensation reaction they give products consisting mainly of esters of polypeptides [2], cyclic dimers (piperazinediones) being present only in very small amount. It was natural, therefore, to pay attention not only to the kinetics of the polycondensation of the glycine esters, but also to the properties of the resulting mixture of polyglycine and piperazinedione. Particular attention was directed to the question of the effect of various factors on the amount of piperazinediones formed. Although there is a considerable literature on this matter [3], there is as yet no clear information on the relative amounts of piperazinediones and polymers in the polycondensation products obtained from esters of α-amino acids. We made use of a recently published procedure [4] for the determination of the amount of piperazinedione in the reaction mixture, and we obtained results of interest not only with respect to glycine esters, but also with respect to esters of other α-amino acids. The main subject of investigation was glycine ethyl ester. Preliminary experiments on other esters of this acid (methyl and butyl) show that the laws of the polycondensation reaction and the identity of the products are similar to those found for the ethyl ester. Only glycine methyl ester differs notably from the other esters: under given conditions its reaction rate is higher, and the amount of polycondensation products is much lower.

EXPERIMENTAL

Glycine ethyl ester was prepared by Fischer's method [5]. In order to obtain reproducible results it is very important to dry the ester thoroughly, since traces of moisture result, as we have shown, in an appreciable increase in the rate of the process studied. In order to remove moisture as completely as possible, the free glycine ester was extracted with absolute ether, and the extract was then dried for 15 days over a large amount of calcined potassium carbonate. The ether was then distilled off, and the residue was distilled under reduced pressure. A fraction of the glycine ethyl ester having a distillation range of 1-1.5° was taken for investigation.

This fraction, which was collected in a separate receiver, was poured into one-hundred times its weight of absolute ether, and was kept over a large amount of calcined potassium carbonate. It was shown that a hundredfold dilution enabled the glycine ester to be preserved almost unchanged for more than two months. Before each experiment a known weight of the ester was taken in the form of 30-40 ml of the solution, from which ether was distilled at atmospheric pressure and the monomer (the glycine ester) was distilled by the method already described [1]. Sealed tubes containing monomer and catalyst (carbon dioxide) were placed in a thermostat at the required temperature. After a period of reaction, the tubes were opened and treated as previously described [1].

The results of the experiments are given in Fig. 1. For comparison, the results for the polycondensation at 40° of glycine ethyl ester that had not been freed from moisture with calcined potassium carbonate are given (Curve I). It will be seen from Fig. 1 that the rate of the polycondensation of the dried glycine ester under the same conditions is appreciably lower (Curve III). It is noteworthy that the reaction rate at the beginning of the process (the first 2-3 hours) is much lower than in the following period (3-5 hours after the start), so that the rate curves have a pronounced inflection (at the third hour).

In order to resolve the question of whether these inflections are the result of some, at present unknown, autocatalytic process, experiments were carried out on the polycondensation of glycine ethyl ester to which polyglycine was added as catalyst. Determinations of the amine nitrogen by the van Slyke method indicated an increase in reaction rate in these experiments by a factor of 1.5-2.

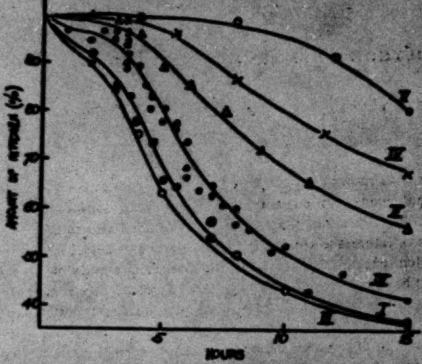


Fig. 1. Dependence of the amount of nitrogen evolved in the van Slyke determination on the duration of reaction for the polycondensation of glycine ethyl ester in presence of 2 mole-% of CO_2: I - 40° with moist ester; II - 30°; III - 40°; IV - 20°; V - 0°

It was of interest to determine the compositions of the polycondensation products obtained in the period before the inflection and in the period after it. By use of the method of determining piperazinediones by hydrolysis with weak alkalis [4], it was shown that in the first stage of the reaction the content of piperazinediones in the reaction mixture attains a value of 53%, whereas at the tenth hour of the reaction (at the same temperature and with the same amount of catalyst) their content is reduced to 11%.

It is interesting that the amount of piperazinedione in the reaction mixture is appreciably dependent on the temperature at which the experiment is carried out. Fig. 2 gives the results of experiments carried out to the same progress of reaction, but at different temperatures. These results show quite clearly that rise in reaction temperature results in an increased yield of piperazinediones in the reaction mixture. This is probably the explanation of the high yield of piperazinediones obtained from esters of α-amino acids by Fischer's method [5], in which it is recommended that the esters be heated to a high temperature (about 180°).

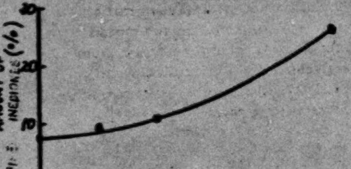


Fig. 2. Dependence on reaction temperature of the amount of piperazinediones found among the polycondensation products from glycine ethyl ester.

The polycondensation products were characterized by their solubilities and melting points.

Particular attention was devoted to the solubility of the polycondensation products in water, since this is of great importance in various chemical and physicochemical investigations (van Slyke determination of amine nitrogen, ionophoresis, chromatography, etc.). The investigations showed that the polycondensation of glycine ethyl ester— which attained a degree of completeness of 90%— yielded products that were only partially soluble in water and gave saturated solutions containing about 2.5% (on the total weight of the solution) of polymers and piperazinediones. The remainder of the polycondensate remained insoluble in water, even at high dilution and when the temperature was raised to 100°. With the object of raising the solubility, we carried out a series of copolycondensations of glycine ethyl ester with ethyl esters of other α-amino acids: DL-alanine, DL-valine, DL-norleucine, DL-phenylalanine, and L-aspartic acid.

A mixture of esters of definite composition was obtained by the successive selection and weighing of first one component and then the next by the method described previously [1].

The tubes containing the binary mixture of monomers were heated at 40° for 30 hours. The tubes were opened, and their contents were ground to a powder in an agate mortar, washed with absolute ether to remove unchanged monomers and alcohol formed in the reaction, and dried over sulfuric acid in a vacuum desiccator. The properties of the products were then investigated.

The results of these experiments show that, as a rule, these products are more soluble in water than the polycondensation product obtained from a single amino ester. Good results were obtained when the second component was DL-alanine ethyl ester. In illustration of the results we give the graph for the composition-dependence of the melting points and solubilities in water at room temperature of the copolycondensation products from the ethyl esters of glycine and DL-alanine (Fig. 3).

A notable feature is the sharp rise in solubility in water (Curve I) as the composition of the original mixture approaches equimolecular proportions, for which the solubility attains 35%. At this point the aqueous solutions obtained do not contain insoluble particles, such as are present in those obtained from polyglycine, but become completely clear when a slight excess of water is added. It will be seen from the same graph that the melting point of the copolycondensation product also changes as the composition of the original mixture is varied (Curve II), falling to 180° at the point representing equimolecular composition. Melting is accompanied by some darkening in color, but there is no decomposition like that occurring during the melting of poly-DL-alanine (m.p. 240°) and, particularly, polyglycine (m.p. 306°), when complete charring occurs, even in a sealed capillary. It is characteristic that an artificially prepared mixture of polyglycine, poly-DL-alanine, piperazinedione, and lactimide does not have a sharp melting point, but chars in the range 240-300°. The solubility of such artificial mixtures in water differs little from that of the polycondensation products obtained from pure glycine ethyl ester.

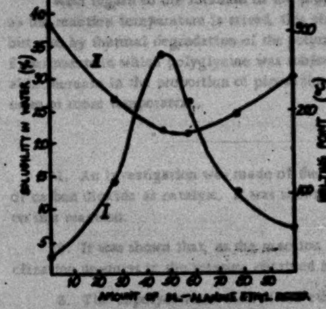
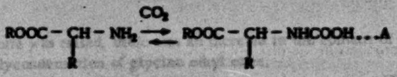


Fig. 3. Dependence of the solubility in water (I) and melting point (II) of a copolycondensation product obtained from the ethyl esters of glycine and DL-alanine on the composition of the original monomer mixture

Discussion of Results

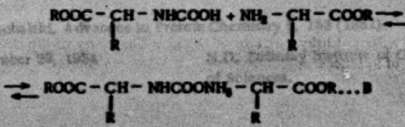
It has been emphasized previously [1] that the catalytic action of acidic catalysts is associated with their ability to yield hydrogen ions, which activate the ester linkage in reactions with other substances and with molecules of the same substance. Carbon dioxide is here able to play the part of an acidic substance, in as much as it forms carbamic acid derivatives with esters of α-amino acids:



$$\underset{\displaystyle R}{\mathrm{ROOC-\underset{|}{CH}-NH_2}} \overset{CO_2}{\rightleftharpoons} \mathrm{ROOC-\underset{\underset{\displaystyle R}{|}}{CH}-NHCOOH\ldots A}$$

(I)

Compounds of the type (I) have been isolated and have been described in the literature [6] as weak unstable acids. The acidic properties of these substances are confirmed by their ability to react with basic compounds, in particular with esters of α-amino acids, to give the corresponding salts (carbamates) (II):

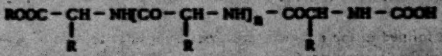


$$\mathrm{ROOC-\underset{\underset{\displaystyle R}{|}}{CH}-NHCOOH+NH_2-\underset{\underset{\displaystyle R}{|}}{CH}-COOR} \rightleftharpoons$$

$$\rightleftharpoons \mathrm{ROOC-\underset{\underset{\displaystyle R}{|}}{CH}-NHCOONH_3-\underset{\underset{\displaystyle R}{|}}{CH}-COOR\ldots B}$$

(II)

The reversibility of the reactions A and B, which has been confirmed by experiment, indicates the complexity of the processes occurring in the reaction mixture yielded by esters of α-amino acids and the probability of the appearance of acidic substances of type (I), able to catalyse the polycondensation of these esters. Moreover, it is possible that carbamic acid derivatives (I) may be formed not only by esters of α-amino acids, but also by their polymers:



$$ROOC-\underset{\displaystyle R}{\underset{|}{C}}H-NH[CO-\underset{\displaystyle R}{\underset{|}{C}}H-NH]_n-CO\underset{\displaystyle R}{\underset{|}{C}}H-NH-COOH$$

(III)

The compounds (III) will clearly have acidic properties and will be able to yield free hydrogen ions, which will activate the ester linkages of neighboring molecules.

It is highly probable that a definite time will be required for the formation of the compounds (III); accordingly, in the initial period (up to three hours) the reaction rate is lower than in the subsequent period (after three hours).

As regards the catalytic effect of moisture on the reaction studied, it must be remembered that water readily hydrolyses ester groupings – both those of the esters of α-amino acids, and also those of the polymers [7] to carboxyl groups. The latter – as shown by the effect of the addition of polyglycine as catalyst – have the usual catalytic effect. It is characteristic that the α-amino acids themselves have no catalytic action on the reaction of the glycine ester.

As regards the increased solubilities and lower melting points of the copolycondensation products formed by glycine ethyl ester with esters of other α-amino acids, these results are in accord with the variations in properties observed in other copolymers [9].

With regard to the increase in the proportion of the piperazinedione component of the reaction mixture as the reaction temperature is raised, this phenomenon may result not only by direct cyclization of dipeptides, but also by thermal degradation of the polymers to dimers followed by cyclization to piperazinedione [10]. Experiments in which polyglycine was subjected to prolonged heating at 100° showed that there was an appreciable increase in the proportion of piperazinedione in products obtained by the polycondensation of glycine ethyl ester at room temperature.

SUMMARY

1. An investigation was made of the kinetics of the polycondensation of glycine ethyl ester in presence of carbon dioxide as catalyst. It was shown that both moisture and also polyglycine itself had catalytic effects on this reaction.

2. It was shown that, as the reaction temperature was raised, there was an increase in the content of cyclization products in the mixture obtained by the polycondensation of glycine ethyl ester.

3. The copolycondensation of the ethyl esters of glycine and DL-alanine was investigated, and the properties (solubility in water, melting point) of theproducts were studied.

LITERATURE CITED

[1] V.V. Korshak, K.T. Poroshin, and T.D. Kozarenko, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, 663 (T.p. 565)*.

[2] E. Katchalski, Advances in Protein Chemistry 6, 153 (1951).

Received December 29, 1954

N.D. Zelinsky Institute of Organic Chemistry of the USSR Academy of Sciences.

[3] M. Frankel, E. Katchalski, J. Am. Chem. Soc. 64, 2264, 2268 (1942); Th. Curtius, Ber. 37, 1284 (1904); E. Fisher 34, 433, 2868 (1901); 39, 473, 2898 (1906; K. Meyer, O.K. Klemm, Helv. chim. Acta 23, 25 (1940); R. Kempf, Journ. prakt. Chem. 78, 243, 258 (1908); N.I. Gavrilov and V.S. Poptsova, Biochem. Z. 271 292 (1934); V.S. Balabukha-Poptsova, N. I. Gavrilov, and A.M. Rikaleva, 283, 62 (1935); V.S. Balabukha and N.I. Gavrilov, Bull. Moscow State Univ. No. 1, 105 (1948); G. Schramm, H. Restle, Die Makrom. Chem. 13, 103 (1954); H. Huang, C. Nieman, J. Am. Chem. Soc., 72, 921 (1950); H. Brockmann, H. Musso, Ber. 87, 581 (1954).

[4] K.T. Poroshin, T.D. Kozarenko, and Yu. I. Khurgin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 773 (T.P. 693)*.

[5] E. Fischer, Ber. 34, 433, 2868 (1901).

[6] M. Frenkel, O. Neufeld, E. Katchalski, Nature 144, 832 (1939).

[7] E. Fischer, Ber. 34, 2868 (1901); 36, 2094 (1903).

[8] G. Bredig, Z. Phys. Chem. 13, 323 (1894).

[9] F. Strastny, Kunststoffe 40, 273 (1950); W.E. Caltin, E.P. Czezwin, R.N. Willey, J. Sci. Polymer 2, 412 (1947); V.V. Korshak and T.M. Frunze, Proc. Acad. Sci. USSR 103, 843 (1955).

[10] Schramm, H. Restle, Die Makrom. Chem. 13, 103, (1954).

Received December 29, 1954

N.D. Zelinsky Institute of Organic Chemistry of the USSR Academy of Sciences

---

* T.p. = C.B. Translation pagination.

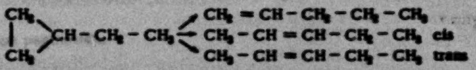
BRIEF COMMUNICATIONS

ISOMERIZATION OF ETHYLCYCLOPROPANE ON SILICA GEL UNDER THE CONDITIONS OF CHROMATOGRAPHIC ADSORPTION ANALYSIS

B.A. Kazansky, V.T. Aleksanyan, M. Yu. Lukina,
A.I. Malyshev, and Kh. E. Sterin

In the preparation of highly pure saturated hydrocarbons it is usual, as a preliminary to distillation through efficient columns, to remove possible impurities by chromatographic adsorption on silica gel. However, experiment shows that silica gel is not always inert toward the substance receiving chromatographic treatment, and it may sometimes act as an isomerizing agent. For example, in an investigation of the behavior of certain terpenes in presence of silica gel under the conditions generally met in the chromatographic separation of mixtures, Arbuzov and Isaeva [1] found that dipentene, pinene, and 3-carene underwent partial isomerization. Among the isomerization products from dipentene they found terpinolene and p-cymene; pinene was partially converted into camphene, dipentene, and terpinolene; and 3-carene was isomerized into dipentene and terpinolene. Dipentene evidently isomerizes by displacement of the double bond, whereas pinene and 3-carene isomerize at the expense of the bridge linkages taking part in three- and four-membered rings. Boord and coworkers [2] found that 1,1,2-trimethylcyclopropane was isomerized in presence of silica gel at room temperature, but the authors did not identify the reaction products. These various observations indicated that it would be of interest to investigate the behavior of monocyclic hydrocarbons of the cyclobutane and cyclopropane series in presence of silica gel, a matter that has not yet been the subject of special study.

We observed recently [3] that isopropylcyclobutane can be filtered through silica gel without undergoing isomerization, and therefore can be purified by this method. When we attempted to purify ethylcyclopropane synthesized by reduction of the hydrazone of cyclopropyl methyl ketone – it was found that unsaturated compounds made their appearance in the hydrocarbon after its contact with silica gel. In order to investigate this phenomenon, we filtered ethylcyclopropane – which had been distilled through an efficient column and, judging by its constants, was very pure – through a layer of silica gel. Investigation of the product with the aid of Raman spectra showed that it contained 2-pentene (in the form of cis and trans isomers) and 1-pentene. Hence, under the influence of contact with silica gel, ethylcyclopropane is partially isomerized into these alkenes:



These results are in accord with the above-mentioned observations on the isomerization of 3-carene, and they permit us to conclude that silica gel is not a suitable sorbent for the chromatographic purification of substances containing a cyclopropane ring.

EXPERIMENTAL

The ethylcyclopropane taken (10.4 g) had b.p. 36.0° (760 mm), n_D^{20} 1.3786; d_4^{20} 0.6840, and aniline point + 17.9° (the literature [4] gives 35.94° (760 mm), n_D^{20} 1.3786; and d_4^{20} 0.6839); it was filtered through a column containing 160 g of silica gel (type: KSM, (a) 14.7). The temperature of the water cooling the silica gel was + 1.7°. The duration of the experiment was ten hours. The product (8.84 g) distilled over at 34.0-36.5° (731.5 mm) and had n_D^{20} 1.3792; and d_4^{20} 0.6740; it immediately decolorized bromine water.

Below, we give the Raman spectrum of the product.

Δν (cm^{-1}; the intensities are given on a 10-point scale): 309 (0,b), 351 (0), 373 (3,b), 410 (2,b), 443 (5,b), 460 (0), 487 (4), 580 (0,b), 624 (0), 707 (0), 725 (1), 749 (7), 766 (1, doublet), 789 (0), 800 (1,b), 818 (5,b), 860 (4), 890 (5,b), 919 (8,sh), 940 (0), 955 (0), 970 (0), 987 (0), 1017 (2), 1033 (4,b), 1054 (2), 1088 (4), 1109 (3), 1129 (0), 1172 (2), 1200 (10), 1243 (2,b), 1266 (2,b), 1289 (3), 1310 (4), 1328 (1,b), 1381 (5), 1428 (3), 1444 (9,b), 1645 (1), 1659 (6,sh), 1675 (8,sh).

For the quantitative determination of the composition of the mixture obtained, we used the spectrum of 1-pentene, which we have determined previously [5], the spectrum of ethylcyclopropene*, and the spectra of the stereoisomeric 2-pentenes. Since the spectra given in the literature for the 2-pentenes were obtained by the photoelectric method, we made an approximate recalculation of the intensities to the cyclohexane scale used in our measurements; the relative error in the determination of the content of 2-pentenes may therefore be somewhat higher than the errors for ethylcyclopropane and 1-pentene.

On the basis of the spectrum results we determined the composition of the mixture to be as follows: ethylcyclopropane 68%, cis-2-pentene 12%, trans-2-pentene 17%, and 1-pentene 3%.

SUMMARY

1. It was found that, when ethylcyclopropane was filtered through a layer of silica gel (the relative weights of hydrocarbon and silica gel being: 1 : 16), 32% of it underwent isomerization.

2. It was shown that the product of the isomerization of ethylcyclopropane consisted mainly of cis- and trans-2-pentenes.

LITERATURE CITED

[1] B.A. Arbuzov and Z.G. Isaeva, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, No. 5, 843 (T.p. 747)*.

[2] R.G. Kelso, K.W. Greenlee, J.M. Derfer, C.E. Boord, J. Am. Chem. Soc. 74, 287 (1952).

[3] B.A. Kazansky, M. Yu Lukina, and L.A. Nakhapetyan, Proc. Acad. Sci. USSR, 101, 683 (1954).

[4] R. Van Volkenburgh, K.W. Greenlee, J.M. Derfer, C.E. Boord, J. Am. Chem. Soc. 71, 172-176 (1949).

[5] P.A. Bazhulin and Kh. E. Sterin, Bull. Acad. Sci. USSR, Physical Series 2, 456 (1947).

[6] M.R. Fenske et al, Anal. Chem., 19, 700, (1947).

Received June 29, 1955

N.D. Zelinsky Institute of Organic Chemistry of the USSR
Academy of Sciences

---

* T.p. = C.B. Translation pagination.

DEPENDENCE OF THE KINETICS OF THE DECOMPOSITION OF CYCLOHEXENE ON THE STRUCTURE OF THE CATALYST

E.K. Mankash and V.V. Shchekin

In the estimation of catalytic activity, the importance of kinetic methods that take account not only of the chemical composition of the catalyst, but also of its physical structure, is being increasingly recognized. The treatment of kinetics in association with the structure of catalysts, and therefore with due consideration of diffusion phenomena, was developed by Zeldovich [1] as early as 1939. The theoretical work of Zeldovich [1], and also of Thiele [2], found its continuation in the work of Wheeler [3], Wagner [4], Hougen and Watson [5], Boreskov [6], and others.

In order to verify the part played by diffusion in its dependence on catalyst structure, we made use of the results of experiments on the transformations of cyclohexene over a series of aluminosilicate catalysts of identical composition but different structures, the temperature being 316° and the space velocity 1 liter/liter · hour. The amount transformed was taken to be the sum of saturated hydrocarbons and polymers calculated as percent by weight on the original raw material. In all cases, since the particle radii of the catalysts did not exceed 100 A, we shall assume Knudsen diffusion [3, 7].

In order to calculate the accessibility of the catalyst surface under the conditions of the reaction studied, we used Wheeler's equation [3], which was derived for the case of heterogeneous unimolecular gas reactions in a stream:

$$h\,\mathrm{th}\,h = \frac{a^2}{18D_k}\,\frac{F}{C_A}\,\frac{1}{\rho v}\,\ln\frac{1}{1-y}, \tag{1}$$

$$\frac{1}{h}\,\mathrm{th}\,h = f, \tag{2}$$

in which $\underline{f}$ is the accessibility, as a fraction of unity,
$\underline{h}$ is a dimensionless parameter,
$\underline{a}$ is the grain diameter of the catalyst (cm),
D_k is the Knudsen diffusion coefficient (cm^2/sec),
C_A is the reactant concentration (mole/cc),
ρ is the density of the catalyst substance (account being taken of the porosity) (g/cc),
$\underline{v}$ is the specific volume of pores (cc/g),
$\underline{y}$ is the fraction of the substance transformed,
$\underline{F}$ is the rate at which the reactant is supplied (moles per cc of catalyst per second).

In an inactive catalyst the reactant molecules may penetrate deeply into the pores before reacting, whereas, when the catalyst is an active one, reaction starts immediately near the entrances of the pores. Hence, the accessibility of the surface is greater for an inactive catalyst than for an active one, and the intrinsic activity of a catalyst, taking the effect of structure into account, is characterized by a rate constant for the given reaction of k_s, which is given by the equation:

$$-\frac{dn}{dt} = k_s C_A^n\,ds, \tag{3}$$

in which $\frac{dn}{dt}$ is the number of moles in each cc reacting per second at a surface of area $\underline{ds}$ in contact with reactant at concentration C_A, and $\underline{n}$ is the order of the reaction.

The temperature-dependence of k_s is in accord with the Arrhenius equation, and, when account is taken of the accessibility, a knowledge of it enables the activation energy to be determined.

Equation 1 can be written

$$h\,\mathrm{th}\,h = zk_v. \tag{4}$$

in which $k_v = \frac{F}{C_A} \ln \frac{1}{1-y}$ is a first-order rate constant referred to unit volume of catalyst (seconds); it depends on the properties of the reactant. The value of $z = \frac{a^2}{18 D_k \rho v}$ is a constant for a given catalyst at a given temperature, and it is determined by the catalyst structure. The parameter h is determined by the ratio of the kinetic and diffusion constants:

$$h = \frac{L}{\sqrt{r}} \sqrt{\frac{k_s}{D_k}}, \tag{5}$$

in which L and r are respectively, the length and radius of the pores (cm).

For high values of h (h 2), the value of f approximates to $\frac{1}{h}$. The parameter h can be regarded as a diffusion-retardation factor, directly proportional to the length of the pores and inversely proportional to their size. When the limiting effect of diffusion is increased, the accessibility of the surface f diminishes. If, taking Equation 1 into account, we replace $h\,\mathrm{th}\,h$ in Equation 4 by its equivalent $h^2 f$, we obtain the relationship between k_v and the accessibility and retardation coefficients f and h:

$$k_v z = h^2 f. \tag{6}$$

It can be seen from Equation 1 that, for constant temperature and a given reaction, $h\,\mathrm{th}\,h$ is directly proportional to a^2 and inversely proportional to D_k and v. When $D_k v < 3 \cdot 10^{-3}$, the value of f rapidly falls and so becomes more and more important. When $D_k v > 3 \cdot 10^{-3}$, the accessibility of the surface is already more than 95%, the part played by diffusion factors rapidly diminishes, and the reaction passes into the kinetic region. Equation 1 and the conclusions derived from it are applicable only in a definite range of values of $h > 0{\cdot}3$, when h is proportional to $\sqrt{\frac{k_s}{D_k}}$, i.e. under kinetic conditions complicated by diffusion. At very high values of h, reaction goes only at the surface, and the process assumes a purely diffusional character. The intrinsic rate constant for the reaction k_s may be found from the equation

$$k_s = \frac{9h^2 r D_k}{a^3}. \tag{7}$$

Substituting the value of h^2 from Equation 7 into Equation 6 we obtain

$$k_v z = f \frac{k_s a^3}{D_k 9 r}. \tag{8}$$

whence

$$\frac{k_v}{f} = k_s \frac{2v}{r} \rho = k_s s_0 \rho \tag{9}$$

or

$$k_v = k_s s_{eff} \rho = k_0 s_0 \rho, \tag{10}$$

in which $k_0 = \frac{k_v W}{S}$; s_0 is the specific surface of the catalyst (sq-cm/g); $s_{eff} = s_0 f$; $\rho = \frac{g}{W}$ (g is the weight, and W the volume of the catalyst).

It should be noted that Equation 1 does not take account of retardation of reaction by chemical causes (e.g. by reaction products, etc.); it provides kinetic relationships determined only by the structure of the catalyst in the region of kinetics complicated by diffusion.

TABLE 1

Structural Characteristics of Catalysts

Catalyst No.	sq·cm/g	cm	cc/g	cm²/sec	$vD_k\ 10^3$
1	665	9,0	0,300	2,35	0,71
2	715	10,0	0,358	2,61	0,93
3	704	10,0	0,352	2,61	0,92
4	667	10,4	0,347	2,71	0,94
5	422	25,1	0,527	6,55	3,45
6	404	47,3	0,953	12,35	11,75
7	308	74,0	1,123	19,32	21,73

TABLE 2

Kinetic Characteristics of Catalysts

Catalyst No.	y	k_v	h	hthh	f	$s_{eff}\cdot 10^{-4}$ (sq·cm/g)	$\frac{1}{\sqrt{\frac{l_s}{D_k}}}\times 10$	$k_s\ 10^3$	$k_o\ 10^3$
1	0.840	0.242	1.49	1.34	0.60	400	6.66	10.50	6.3
2	0.800	0.213	1.15	0.94	0.715	512	5.45	7.78	5.6
3	0.733	0.174	1.02	0.77	0.77	542	4.85	6.12	4.8
4	0.767	0.192	1.05	0.82	0.75	497	5.0	6.76	5.1
5	0.603	0.125	0.40	0.14	0.95	399	3.0	5.96	5.7
6	0.493	0.09	0.108	0.031	0.99	400			
7	0.233	0.035	0.04	0.007	1.00	308			

As can be seen from Tables 1 and 2, Experiments 6 and 7 were carried out in the kinetic region with complete accessibility to catalyst.

SUMMARY

1. With the transformation of cyclohexene over aluminosilicate catalysts varying in structure taken as example, it has been shown that the kinetic method of assessing catalyst activity from rate constants that take retardation by diffusion into account (k_s) is applicable to such transformations.

2. It was shown that the value of the dimensionless parameter h is a characteristic of the extent of diffusional retardation, being proportional to the ratio of kinetic and diffusion rates.

3. It was shown that the value of the reaction rate constant k_o does not depend on the surface area.

4. Wheeler's equation was transformed into a simple form of relationship between the constants k_v, k_o, and k_s and the value of the effective (accessible) surface, i.e. the physical properties of the catalyst.

LITERATURE CITED

[1] Ya. B. Zeldovich, J. Phys. Chem. 13, No. 2, 163 (1939).

[2] E.W. Thiele, Ind. Eng. Chem. 31, No. 7 (1939).

[3] A. Wheeler, Advances in Catalysis 3, 250 (1951).

[4] C. Wagner, Z. Phys. Chem. A193, 1 (1943).

[5] O.H. Hougen, K.M. Watson, Ind. Eng. Chem. 35, 535 (1943).

[6] G.K. Boreskov, V.A. Dzisko, and M.S. Borisova, J. Phys. Chem. 28, No. 6, 1958 (1954).

[7] C. Bokhoven, J. Hoogschagen, J. of Chem. Phys. 21, No. 1, 159 (1953).

Received June 10, 1955

Petroleum Institute of the USSR Academy of Sciences.

SYNTHESIS AND PROPERTIES OF (1-CYANO-1-METHYLETHOXY) SILANES

A.D. Petrov, V.F. Mironov, and V.M. Vdovin

Organosilicon compounds in which 1-cyano-1-methylethoxy groups are attached to the silicon atom are of interest on account of the stability of this group to hydrolysis [1]. The properties of these compounds are similar to those of compounds containing highly branched aliphatic radicals attached to a silicon atom, not only through oxygen, but also through NH and sulfur [2]. However, unlike the latter compounds, (1-cyano-1-methylethoxy) silanes, and methods for their synthesis, have as yet received very little study.

Compounds of this type were first prepared from chloromethylsilanes and acetone cyanohydrin (2-methyllactonitrile) by Frisch and Wolf [1], who also established their stability to hydrolysis and noted the absence of any odor of hydrocyanic acid.

However, Hahn [3], who also synthesized similar compounds from silicon tetrachloride and the cyanohydrins of acetone and other ketones, states that the hydrolysis of these compounds is accompanied by an odor of hydrocyanic acid. In the present investigation we have prepared some new (1-cyano-1-methylethoxy) silanes by reaction in accordance with Scheme 1 between acetone cyanohydrin and alkyl-or aryl-chlorosilanes, and we find that these substances do not eliminate hydrogen cyanide in the course of hydrolysis or during storage:

$$1.\ R_nSiCl_{4-n} + (4-n-m)\ HOC(CH_3)_2CN \xrightarrow{\text{pyridine}}$$
$$\rightarrow R_nSiCl_m[OC(CH_3)_2CN]_{4-n-m},$$

in which $R = CH_3$, C_2H_5, C_6H_5, H, CH_2Cl, $CHCl_2$; $n = 0\text{-}3$; $m = 0\text{-}2$.

It is noteworthy that $[NCC(CH_3)_2O]_4Si$ is very readily formed from silicon tetrachloride and acetone cyanohydrin (55.6% yield), whereas the syntheses of (tert-$C_4H_9O)_4Si$ and (tert-$C_4H_9NH)_4Si$ require very severe reaction conditions [4, 6]. In this reaction, apart from (1-cyano-1-methylethoxy) silanes, we obtained 2-5% of higher-boiling compounds, the analyses and molecular refractions of which indicate them to be the corresponding disiloxanes, formed as a result of the hydrolysis of Si—Cl bonds, probably by water eliminated from acetone cyanohydrin.

EXPERIMENTAL

We describe the syntheses of the two compounds $R_2Si[OC(CH_3)_2CN]_2$ and $RCl_2Si[OC(CH_3)_2CN]$. The rest of the compounds listed in the table were synthesized in an analogous manner; the relative amounts of reactants and conditions of synthesis were the same for Compound 9 (see table) as for Compound 2.

Dichloro (1-cyano-1-methylethoxy) ethylsilane $(C_2H_5)Cl_2Si[OC(CH_3)_2CN]$. Acetone cyanohydrin (59 g, i.e. 0·7 mole) was added over a period of three hours to a cooled stirred mixture of 342 g (2.1 moles) of $C_2H_5SiCl_3$, 56 g of pyridine, and 500 ml of benzene. After one day pyridine hydrochloride was filtered off and washed with two 100-ml portions of benzene. Benzene and $C_2H_5SiCl_3$ were distilled off, and vacuum distillation of the residue yielded four fractions:

Fraction I, B.p. 30 − 76° (8mm); 24 g
Fraction II, B.p. 77 − 80° (9mm); 84 g
Fraction III, B.p. 80 − 138° (15mm); 5 g
Fraction IV, B.p. 138 − 143° (15mm); 11 g

Fractions II and IV were found to be Compounds 6 and 7, respectively (see table).

TABLE

No.	Formula of substance	Yield (%)	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	Molecular refraction		Analysis for Si (%)	
						Found	Calculated [5]	Found	Calculated
1	$(CH_3)HSi[OC(CH_3)_2CN]_2$	72,2	108(14mm)	1,4130	0,9644	54,90	54,97	13,20; 13,16	13,21
2	$(C_2H_5)_2Si[OC(CH_3)_2CN]_2$	60,3	141-2 (19mm)	1,4270	0,9576	68,20	68,36	10,62; 10,98	11,03
3	$(C_6H_5)CH_3Si[OC(CH_3)_2CN]_2$	81	153-4 (4mm)	1,4780	1,0327	79,05	79,16	9,91; 9,83	9,77
4	$(ClH_2C)CH_3Si[OC(CH_3)_2CN]_2$	77,5	114 (3mm)	1,4380	1,0702	63,94	64,15	10,38; 10,01	10,75
5	$(Cl_2HC)CH_3Si[OC(CH_3)_2CN]_2$	40,8	139 (3mm)	1,4462	1,1374	69,22	69,11	–	–
6	$(C_2H_5)Cl_2Si[OC(CH_3)_2CN]$	55,6	78 (9mm)	1,4268	1,1211	48,76	48,58	13,39; 13,61	13,28
7	$(C_2H_5)ClSi[OC(CH_3)_2CN]_2$	11,8	139-140 (15mm)	1,4320	0,9735	–	63,46	10,77; 10,72	10,76
8	$(C_6H_5)Cl_2Si[OC(CH_3)_2CN]$	82,2	116 (2mm)	1,4996	1,1915	64,41	63,89	10,87; 10,75	10,78
9	•$[NCC(CH_3)_2O]_4Si$	55,8	m.p. • 92-94° C without recrystallization					7,28; 7,44	7,66

• The literature [3] gives m.p. 96°, yield 3.0%.

Bis(1-cyano 1-methylethoxy)methylphenylsilane

$(CH_3)C_6H_5Si[OC(CH_3)_2CN]_2$. To a cooled stirred mixture of 80 g (1 mole) of pyridine, 85 g (1 mole) of acetone cyanohydrin, and 150 ml of benzene, 96 g (0.5 mole) of $CH_3(C_6H_5)SiCl_2$ was added over a period of 30 minutes. After one day the precipitate formed was filtered off and washed with benzene. Vacuum distillation yielded four fractions:

Fraction I, B.p. 20-149° (4 mm); 17 g
Fraction II, B.p. 149-156° (4 mm); 115 g
Fraction III, B.p. 155-200° (4 mm); 2 g
Fraction IV, B.p. 200-203° (3 mm); 3.5 g

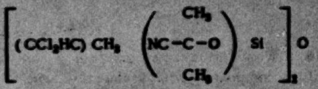
Fraction II was found to be Compound 3 (see table). Fraction IV had n_D^{20} 1.4800 and d_4^{20} 1.0645, and was probably $[CH_3C_6H_5(NC-\underset{CH_3}{\overset{CH_3}{C}}-O)Si]_2O$; found MR 113.30, calulated MR 117.52.

Found %: Si 13.09, 13.22
$C_{12}H_{28}N_2Si_2O_3$. Calculated %: Si 12.67

Similar fractions were obtained in the synthesis of Compound 2, b.p. 153-154° (5 mm); n_D^{20} 1.4332; d_4^{20} 0.9734; Found MR 95.23 for $[(C_2H_5)_2(NC-\underset{CH_3}{\overset{CH_3}{C}}-O)Si]_2O$; calculated 95.42.

Found %: C 53.86; 53.80
H 8.85; 8.92
Si 14.80; 14.58
$C_{16}H_{32}N_2Si_2O_3$. Calculated %: C 53.89
H 9.04
Si 15.71

In the synthesis of Compound 5 we obtained a substance having b.p. 176-178° (1 mm); n_D^{20} 1.4563; d_4^{20} 1.2052; found MR 98.91; calculated 97.22; it was probably

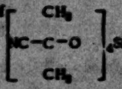


$$\left[(CCl_2HC)\,CH_3\left(NC-\underset{CH_3}{\overset{CH_3}{C}}-O\right)Si\right]_2O$$

SUMMARY

1. A study was made of the reactions of acetone cyanohydrin with chlorosilanes containing methyl, ethyl, phenyl, chloromethyl, and dichloromethyl substituents, and including also silicon tetrachloride.

2. It was found that steric hindrance was absent in the synthesis of



$$\left[NC-\underset{CH_3}{\overset{CH_3}{C}}-O\right]_4Si$$

from silicon tetrachloride and acetone cyanohydrin.

LITERATURE CITED

[1] K. C. Frisch, W. Wolf, J. Org. Chem. 657 (1953).

[2] C. S. Moner, V. Bryan, G. W. Pedlow, Ind. Eng. Chem. 39, 1368 (1947); G. W. Pedlow, C. S. Miner, US Pat. 2566364 (1951); C. A. 46, 3068 (1952).

[3] W. Hahn, Makromolekulare Chem. 11, No. 1, 64 (1953).

[4] H. Breederveld, H. J. Watermann, Research 6, 485 (1953); Abstr. J. (Chem.), No. 8, 23445 (1954). Réc. , trav. chim., 73, No. 11, 871 (1954), Abstr. J. (Chem), No. 13, 26247 (1955).

[5] R. L. Warrick, J. Am. Chem. Soc. 68, 2455 (1946).

[6] J. F. Hyde, J. W. Curry, J. Am. Chem. Soc. 77, 3140 (1955).

Received August 6, 1955

N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences.

ORGANOBORON COMPOUNDS

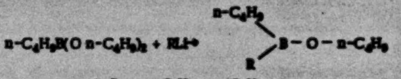
COMMUNICATION 4. SYNTHESIS OF DIALKYLBORINIC ESTERS WITH THE AID OF LITHIUM REAGENTS

B.M. Mikhailov and T.A. Shchegoleva

Several methods are known for the synthesis of dialkylborinic esters, but they are all of limited application. For example, diethylborinic esters can be prepared by the action of aldehydes on triethylborine [1], and butyl dibutylborinate has been prepared by the oxidation of tributylborine with moist air [2]. These methods have not been extended to the preparation of other borinic esters. A more general method is that based on reaction between an alkyl magnesium halide and butyl ethylene borate [3], by means of which ethylene bis(dibutylborinate) and ethylene bis(diisopentylborinate) have been prepared in 45-47% yield. However, like the previous methods, this method does not enable us to prepare borinic esters in which two different hydrocarbon radicals are attached to boron.

A promising method for the synthesis of esters of this last type is one based on the use of organolithium compounds. One of us, in collaboration with Aronovich, found [4] that organolithium compounds react smoothly with areneboronic esters with formation of diaryl– and alkylaryl-borinic esters. In the further development of this synthesis of organoboron compounds we found that dialkylborinic esters can be synthesized in good yield by the action of alkyllithiums on alkaneboronic esters. This method enables us to prepare not only those borinic esters in which the alkyl radicals on the boron are identical, but also the previously inaccessible esters in which the alkyl radicals are different.

The present paper describes the preparation of the butyl esters of dibutyl - and butylpropyl-borinic acids by the action of butyllithium and propyllithium, respectively, on dibutyl 1-butaneboronate:



$$n\text{-}C_4H_9B(O\,n\text{-}C_4H_9)_2 + RLi \rightarrow \begin{matrix} n\text{-}C_4H_9 \\ R \end{matrix}\!\!>B-O-n\text{-}C_4H_9$$

$R = n\text{-}C_4H_9;\ n\text{-}C_3H_7$

EXPERIMENTAL*

Butyl Dibutylborinate. Over a period of one hour at – 70°, a solution of 53 g (0.25 mole) of dibutyl 1-butaneboronate in 50 ml of ether was added to a stirred solution of butyllithium, prepared at 0° from 43 g (0.31 mole) of butyl bromide and 4.17 g (0.6 mole) of lithium in 225 ml of ether. The reaction mixture was stirred for a further four hours at the same temperature and was then set aside overnight. On the next day dry hydrogen chloride was passed until the reaction mixture was saturated, the ether was distilled off, and the precipitate of lithium halides was filtered off. The precipitate was washed with benzene, and solvent and butyl alcohol were vacuum-distilled from the filtrate and washings; precipitate that formed was again filtered off. The resulting liquid was distilled through a 20-cm column. The product was 36.5 g (74.5%) of butyl dibutylborinate, b.p. 122-124° (33 mm) and d_4^{20} 0.8077.

Found %: B 5.62

$C_{12}H_{27}BO$. Calculated %: B 5.46

The reported boiling point of butyl dibutylborinate is 120-121° (24 mm) [2].

Butyl Butylpropylborinate. Reaction between 0.25 mole of dibutyl 1-butaneboronate and 0.25 mole of propyllithium was carried out under the conditions described above. The product was 25.4 g (57%) of butyl butylpropylborinate, b.p. 84-86° (10 mm), d_4^{20} 0.7888.

---

* All operations were carried out in an atmosphere of nitrogen.

Found %: C 71.47; H 13.75; B 5.91

$C_{11}H_{25}BO$. Calculated %: C 71.75; H 13.60; B 5.88

SUMMARY

Treatment of alkaneboronic esters with alkyllithiums yields dialkylborinic esters.

LITERATURE CITED

[1] H. Meerwein, G. Hinz, H. Majert, H. Sönke, J. prakt. Chem. 147, 228 (1936).

[2] J. Johnson, M.G. Van Campen, J. Am. Chem. Soc. 60, 121 (1938).

[3] R. Leitzinger, J. Skoog, J. Am. Chem. Soc. 76, 4174 (1954).

[4] B.M. Mikhailov and P.M. Aronovich, Bull. Acad. Sci. USSR, Div. Chem. Sci. AH CCCP 1955, No. 5, 946 (T.p. 859)* .

Received June 15, 1955

N.D. Zelinsky Institute of Organic Chemistry of the
USSR Academy of Sciences

---

* T.p. = C.B. Translation pagination.

CURRENT EVENTS

GENERAL MEETING OF THE DIVISION OF CHEMICAL SCIENCES OF THE USSR ACADEMY OF SCIENCES ON THE PEACEFUL USES OF ATOMIC ENERGY[*]

On July 2-5, 1955, after the plenary session of a general meeting of the Academy of Sciences of the USSR devoted to a discussion of the peaceful uses of atomic energy, there was a session of the Division of Chemical Sciences of the Academy of Sciences at which chemical aspects of the same subject were discussed. The meetings of the session were held in the large auditorium of the Chemistry Department of the M.V. Lomonosov State University, Moscow, and they were well attended by Soviet scientists.

The following foreign guests took part in the work of the session: Prof. T. Padenrecht[**] and Prof. T. Silmland[**] from Norway; Prof. S. Claesson from Sweden; Prof. E. Leibnitz from the German Democratic Republic; Prof. J.H. de Boer from Holland; Prof. J. Maly from Czechoslovakia; Prof. D. Grdenic and Prof. P. Savic from Yugoslavia; Prof. D. Shankar from India; Prof. E. Schmidt and Prof. B. Karlik from Austria; and Prof. Horna Holubei[**] from Rumania. When opening the first meeting of the session, the chairman, Academician M.M. Dubinin, presented the foreign guests, who were warmly welcomed by the participants.

The first day of the session was devoted to problems in radiation chemistry. V.L. Karpov, Cand. Chem. Sci., read a paper entitled "Action of Nuclear Radiations on High Polymers" (the paper was written conjointly with Academician V.A. Kargin, and B.N. Zvereva, I.Ya. Petrova, and N.A. Slovokhotova also participated in the work). The speaker pointed out that the problem studied is of interest in connection with the use of plastics, rubbers, etc. in presence of high-energy radiation. He pointed out also that the irradiated material might undergo desirable changes of properties under such conditions — for example, change into an infusible, insoluble condition ("radiational vulcanization"), into a state of chemical unsaturation, or into a form of lower molecular weight. The study of such processes may be of interest also for the understanding of the action of ionizing radiations on biological systems, such as proteins, polypeptides, etc.

The results of the investigations show that three main types of processes are to be observed in presence of nuclear radiations: degradation, cross linking of molecular chains, and far-reaching decomposition with formation of gaseous products, the relative extents to which these processes occur being mainly dependent on the chemical nature of the polymer and its molecular structure. The type and energy of the radiation play a very much smaller part: α-particles, fast electrons, and γ-rays produce qualitatively identical changes in a polymer of a given type.

N.A. Bakh, Doctor Chem. Sci., read a paper entitled "Action of Ionizing Radiations on Aqueous Solutions of Inorganic Salts". The speaker remarked that it is not yet fully clear what oxidation and reduction reactions occur in aqueous solutions of inorganic salts under the action of ionizing radiations and in what way these reactions are interrelated. As a result of the interaction of the primary products of the radiolysis of water among themselves and with the original components of the system — cations, anions, and dissolved gases - new components appear, and these, in their turn, take part in reactions — both radiation-induced reactions, and also in thermal reactions. The radiation-induced reactions occurring in aqueous solutions of iron salts, potassium iodide, and sodium nitrate were examined. The irradiation was carried out in glass apparatus designed in various ways, so that the reactions occurring in the systems could be investigated both during the irradiation and after irradiation had ceased. In the main, X-rays of about 90 kv hardness were used, and the dosages ranged up to 2000 roentgens per second. A study was made of the dependence of the observed effects on concentration, pH of the solution, and the identities of the dissolved gases (present at saturation concentration) for various overall doses.

---

[*] The papers read at this conference are available in Consultants Bureau English Translation.

[**] Spelling of these names rendered phonetically from Russian.

A paper entitled "Sensitization and Suppression of Oxidation-Reduction Reactions Occurring During Radiolysis" was read by M.A. Proskurnin, Cand. Chem. Sci., who wrote the paper in collaboration with V.D. Orekhov and E.V. Barelko. The speaker stated that, in the utilization of the energy of nuclear radiation for bringing about chemical processes, it is very important to determine the yields of the radiation-induced reactions that will occur under the given conditions. He maintained that, without a clear understanding of the mechanisms of the processes leading to the sensitization of desirable reactions and the suppression of undesirable reactions, we cannot hope for success in the development of radiation-induced processes.

In a paper entitled "Regularities Observed in the Mechanism and Kinetics of Simple Radiation-induced Reactions (Formation of Ozone and Oxidation of Nitrogen)", S. Ya. Pshezhetsky pointed out that it is important to determine the distinguishing features of radiation-induced reactions, considered in their relation to thermal and photochemical reactions, and to establish their specific laws. The speaker presented some data for two reactions in which simple molecules take part: the formation of ozone and the oxidation of nitrogen, the radiation used being γ-rays from Co^{60}, 200-300-kev electrons, and electrons having an energy of a few hundred electron-volts. Both reactions were studied in the gas and liquid phases, and in both cases charge-transfer processes occur in collisions of ions with atoms and molecules, excited species undergo deactivation processes, and the recombination of atoms and other reactions occur in the reaction space and at the walls. The results presented by this speaker indicate the probable direct participation of ions in radiation-induced reactions — they may, in fact, play a very important part.

On the second day, the session of the Division of Chemical Sciences, with Academician A.P. Vinogradov in the chair, considered matters relating to the action of high-energy particles on atomic nuclei.

A paper on nuclear fission reactions due to negative pions and fast protons was read by N.A. Perfilov, Doctor Phys. Math. Sci., whose co-authors were N.S. Ivanova, O.V. Lozhkin, V.I. Ostroumov, and V.P. Shamov.

The interaction of slow negative pions with nuclei from the end of the periodic system was investigated by the method of thick-layer photographic plates. Experiments were carried out on U, Bi, and W nuclei, which have differences in charge of 9 and 18 units. Nuclear fission reactions due to 460-Mev and 660-Mev protons were also studied by the same method.

The numerous experiments carried out by the authors have enabled them to extend the existing concepts of the mechanism of fission processes and have shown that excitation energy does not pass into the kinetic energy of the fission fragments. An analysis of uranium fissions shows that the nucleus undergoing fission emits approximately as many charged particles (and therefore as many neutrons) as it would be expected to emit on the assumption that the whole of the excitation energy is removed by evaporation of neutrons and charged particles. The authors consider, however, that the agreement found between the experimental and calculated values is not an indisputable proof of purely emissional fission, since different variants of the theory of evaporation may give somewhat different values for the number of charged particles. An analysis of bismuth fissions shows that, as a result of the preliminary "cooling" process, the excited nucleus emits neutrons and charged particles in such numbers that the fission parameter Z^2/A rises to the value at which the fission value is lowered to the binding energy of the neutrons of the residual nucleus. A similar analysis for tungsten showed that fission occurs from a level somewhat above the level for emissional fission, but, as in the cases of uranium and bismuth, after preliminary cooling with emission of a considerable number of neutral and charged particles. The speaker remarked that, in order to create a complete theory of fission, it is essential that further investigation be made into the details of fission processes.

V.I. Baranov, Doctor Phys. Math. Sci., whose co-authors were Academician A.P. Vinogradov, I.P. Alimarin, Corr. Memb. Acad. Sci. USSR, A.K. Lavrukhina, T.V. Baranova, F.I. Pavlotskaya, A.A. Bragina, and Yu. V. Yakovlev, reported on a radiochemical investigation of the fission of bismuth, thorium, and uranium with 480-Mev protons The main object of the investigation was the determination of the laws relating the yield distributions of the various fission products to the identity and energy of the bombarding particle, and also the discovery of new isotopes obtained by bombardment with high-energy protons. The investigation enabled the authors to present a general picture of the nuclear processes occurring. Formation of light nuclei, fission processes, and spallation processes were observed. It was shown that the yield distribution of the fragments with respect to mass number is symmetrical and has a single broad maximum, and it was pointed out that the characteristic features of the fission processes of uranium and thorium resulting from the action of particles of various energies are identical. These peculiarities are also features of the fission processes of other heavy elements. It was stated that the fission of bismuth is preceded by the emission of, on the average, 2 protons and 16 neutrons, a fact that indicates that emmisional fission occurs.

V.N. Mekhedov, Cand. Chem. Sci., whose co-authors were B.V. Kurchatov, M. Ya. Kuznetsova, and L.N. Kurchatova, described a radiochemical investigation of the fission of tungsten with 280-Mev deuterons. A sample of tungsten trioxide was specially purified for the experiments, and this was irradiated in the deuteron beam for one hour. After the irradiation the various radioactive isotopes were separated out on suitable carriers. Altogether, 28 radioactive isotopes – mainly in the range Z = 33-52 were isolated and studied. In addition, calcium, nickel, antimony, and cesium were isolated, but the low activities of the samples did not permit reliable identification of the isotopes formed.

Energy considerations indicated that for 280-Mev deuterons an evaporation mechanism cannot result in the formation of the isotopes found, which differed from tungsten by 40 or more units of mass. It must be considered, therefore, that the products obtained resulted from the fission of tungsten nuclei. The formation cross section for individual isotopes in the region of the yield maximum was found to be about 10^{-28} sq. cm, which is not in conflict with the total fission cross section of tungsten ($\sigma = 1.1 \cdot 10^{-27}$ sq. cm).

B.V. Ershler, Doctor Chem. Sci. (co-authors: G.M. Kukavadze, M.P. Anikina, and L.L. Goldin), discussed the yields of various neodymium and cerium isotopes in the fission of uranium-233. A sample of U^{233} was irradiated for a long time in a nuclear reactor, after which it was set aside for six months and then dissolved, together with its platinum envelope, in aqua regia. The rare earths were separated on an yttrium carrier and subjected to mass-spectrometric analysis. The yields (%) were: Ce^{140} – (5. 6 ± 0.17); Ce^{142} – (5. 6 ± 0.17); Nd^{143} – (5.15 ± 0.3); Nd^{144} – (3.37 ± 0.3); Nd^{145} – (3.00 ± 0.2); Nd^{146} – (2.34 ± 0.15); Nd^{148} – (1.15 ± 0.10); Nd^{150} – (0.51 ± 0.04)%.

A.K. Lavrukhina, Cand. Chem. Sci. (co-authors: Academician A.P. Vinogradov, I.P. Alimarin, Corr. Memb. Acad. Sci. USSR, V.I. Baranov, T.V. Baranova, and F.I. Pavlotskaya) described a radiochemical investigation of the spallation of copper and bismuth nuclei with high-energy particles. The object of the investigation was the determination of the main peculiarities of the spallation process in light and heavy nuclei and the effect of the kind and energy of the bombarding particles on the character of the process. From the character of the spectra of the radioactive nuclei formed, it was possible to show that a great variety of nuclear processes, occur when copper and bismuth are bombarded with 480-Mev protons, namely, emission of light nuclei, nuclear fission and spallation, and secondary reactions leading to the formation of nuclei of atomic number higher than that of the original nucleus. The application of the method of extrapolation and interpolation to the determination of the yields of short-lived and stable nuclei enabled the authors to obtain a complete picture of the yields of spallation products obtained from copper irradiated with 680-Mev protons, to determine the total cross section for the spallation process, to establish the position of the region of nuclei obtained in maximum yield, and to estimate the proportion of stable isotopes in the spallation products of copper.

A.N. Murin, Doctor Chem. Sci., who collaborated with B.K. Preobrazhensky, I.A. Yutlandov, and M.A. Yakimov, read a paper on the spallation and fission reactions of complex nuclei (Cu, La, Bi) bombarded with 480-Mev and 660-Mev protons. Targets of the chemically pure elements or their oxides were used, and these were irradiated with protons in the internal beam of the synchrocyclotron of the Institute of Nuclear Problems of the USSR Academy of Sciences. The reaction products were isolated on inert carriers by the usual methods. The authors established that in all cases the main bulk of the reaction products were formed by a spallation process, i.e. by cascade ejection of nucleons from the target nucleus and subsequent evaporation of protons, neutrons, and α-particles. In the process of evaporation from the excited nuclei, neutrons predominate over charged particles.

The determination of the yields of spallation products enabled the authors to make an approximate estimate of the average excitation energy of the intermediate nuclei, which are formed as a result of a nuclear-cascade process and which emit nucleons and α-particles by evaporation. In this way the mean excitation energy for bismuth was found to be of the order of 90 Mev. The speaker stated that reaction products that are comparatively distantly removed with respect to Z and A from the irradiated nucleus (such as calcium in the irradiation of copper) are probably formed by a mechanism differing from that of the formation of nuclei that are not far-removed from the target nucleus. The yields of Co^{56} from Cu^{63} [Cu^{63}(p; 3 p, 5 n) Co^{56}] and Co^{58} from Cu^{65} [Cu^{65}(p; 3 p, 5 n) Co^{58}]and also of Mn^{56} from Cu^{65} and Mn^{54} from Cu^{63} are very close in value, whereas the yields of Ca^{47} [Cu^{65} (p; 4α, 2p, n) Ca^{47}] and Ca^{45} [$Cu^{[illegible]}$ (p; 4α, 2p, n) Ca^{45}] differ very greatly. The radioactive isotopes Ce^{134} (T = 2.2 days) and $Cs^{[illegible]}$ (T = 2.5 minutes) were first detected in these experiments.

B.V. Kurchatov, Cand. Chem. Sci., whose co-authors were V.N. Mekhedov, N.I. Borisova, M. Ya. Kuznetsova, L.N. Kurchatova, and L.V. Chistyakov, gave a paper entitled "Radiochemical Investigation of the Products of the Spallation of Silver with High-energy Particles", which described the results of a study of the nuclear reactions occurring when silver is irradiated with 550-Mev α-particles, 280-Mev deuterons, and 480-Mev protons. The metallic silver used in this work was extremely pure. About 70 products of the spallation of silver were detected, and the following previously unknown isotopes were estimated and investigated: Cd^{104}, $Cd^{[illegible]}$, $Ag^{[illegible]}$, $Mo^{[illegible]}$, $Sr^{[illegible]}$, $Sr^{[illegible]}$, $Rb^{[illegible]}$.

The last day of the session, which was under the chairmanship of Academician I.I. Chernyaev, was devoted to the application of isotopes in chemical investigations.

A.I. Brodsky, Corr. Memb. Acad. Sci. USSR, devoted his review paper to the investigation of the structures and reactivities of compounds with the aid of isotopes. He emphasized that the study of isotopic exchange provides direct information on the mobilities of atoms in molecules and the dependence of mobility on structure, and it enables us to make a closer approach than can be made by any other method to the solution of a problem that is of the greatest importance for theoretical chemistry – the relationship of reactivity and reaction mechanisms to chemical structure. The speaker referred to the suggestion he made in 1949 to the effect that the peculiar features of exchange at different X–H bonds are associated with the state of the electron shell of the reaction center – in this case the atom X. A.I. Brodsky later developed these ideas in greater detail and confirmed them experimentally. When the atom X has a free (unshared) pair of electrons, deuterium becomes attached by this pair and a proton is simultaneously released from another pair. Exchange of this type is immeasurably fast, irrespective of the structural peculiarities of the molecules, the protolytic properties of the medium, and the presence of catalysts. When there is no free pair on the atom X, the deuteron can become attached only by the pair that was originally binding the proton. This process, unlike the previous one, requires a comparatively high activation energy, and exchange occurs only under favorable conditions, created either by the effect of substituents on the electron density around the atom X and on the strength of the bond X–H, or by strongly acid or basic donors or catalysts. It is generally considered that such exchange proceeds via electrolytic dissociation; an example is found in hydrogen exchange at C–H bonds in various organic compounds. The results of investigations discussed by the speaker enabled him to conclude with reasonable certainty that tautomerism is absent in H_3PO_3, phosphites, and hypophosphites, but present in H_3PO_2, which is as yet the only proved example of tautomerism in inorganic compounds. With the aid of radioactive sulfur it was confirmed that, as suggested by A.E. Arbuzov, the rearrangement of diethyl sulfite into ethyl ethanesulfonate is irreversible.

In a discussion of hydrogen mobility and hydrogen exchange in organic compounds, the speaker examined possible reaction mechanisms: ionization and electrophilic mechanisms, and also exchange by the formation of a nucleophilic fourfold complex with displacement of electrons to hydrogen (deuterium) or with intermolecular transfer of hydride ions.

The speaker cited also the results of investigations by A.N. Nesmeyanov and coworkers, and also by other workers, on the effect of σ-π-conjugation and the mutual orientation of bonds on the reactivity of hydrogen in organic compounds.

A.I. Brodsky discussed also the dependence of oxygen exchange on molecular structure, the mechanism of halogen exchange, the structure of complex inorganic molecules, and other topics.

A.A. Grinberg, Corr. Memb. Acad. Sci. USSR, devoted his review paper to the investigation of the structures and reactions of complex compounds by the method of labeled atoms. He stated the most important of the conclusions that can be drawn from the results of the investigation of these matters by Soviet and foreign workers. He pointed out that the stability of complex compounds (characterized by the value of the instability constant) by no means always determines the rate at which exchange occurs. For example, the bivalent platinum compounds studied, though the most stable in the sense of secondary dissociation, were the most labile from the point of view of kinetics. Further investigations carried out by the speaker and his coworkers showed that the relationship between the exchange rate and the nature of the anion, as found for bivalent platinum compounds, can be extended, in the main, to quadrivalent platinum compounds. The speaker described recent experiments on the rate of isotopic exchange in palladium systems in which exchange was so rapid that the kinetics could not be studied by the usual methods. On the other hand, in an iridium system at concentrations of the order of $10^{-3} - 10^{-3}$ molar, exchange was almost absent. The speaker discussed recent experiments by Ya. A. Fialkov and coworkers on the exchange of SO_4^{2-} between the outer and inner spheres in green chromisulfate complexes, and also the work of V.I. Spitsyn and coworkers on iso- and hetero-poly acids.

G.P. Mikhukhin, Doctor. Chem. Sci., discussed the mobility of sulfur in sulfur-carbon bonds and the mechanism of the action of rubber-vulcanization accelerators. He concluded that, in the majority of cases, the compounds having the most mobile sulfur atoms are at the same time also the most effective accelerators for the vulcanization of rubber. Thus, in presence of potassium ethylxanthate the vulcanization of rubber proceeds at room temperature, dithiocarbamates are accelerators for vulcanization under mild conditions, Captax is a typical accelerator for hot vulcanization, and so on. The speaker emphasized the great importance of the investigation of the exchange reactions of sulfur in organic compounds for the elucidation of a number of problems in sulfur chemistry and, in particular, for the establishment of the mutual effects of atoms and the effect of σ,π-conjugation on the mobility and reactivity of sulfur in various compounds.

A closely related theme was treated by E.N. Guryanova, Cand. Chem. Sci., who read a paper entitled "Sulfur Exchange in Polysulfides and in Various Vulcanization Accelerators" (co-authors: V.N. Vasilyeva and L.S. Kuzina).

V.I. Kuznetsov, Doctor Chem. Sci., discussed the use of organic coprecipitants in analytical chemistry. He stated that organic coprecipitants, like the inorganic agents, are able to precipitate micro quantities of elements quantitatively from extremely dilute solutions of the latter – for example, 10^{-6} g of the element from a volume of several liters. Organic coprecipitants, however, have certain characteristic features: they can be removed from precipitates by simple ignition, they are almost devoid of any tendency to adsorb inorganic ions, they are highly specific in action, their range is almost unlimited, and so on.

The speaker examined the coprecipitation of elements in the form of normal salts, in the form of complex and internal-complex compounds formed by the action of organic reagents, and under some other conditions.

V.I. Kuznetsov emphasized that the study of the theory and the development of the application of organic coprecipitants are impossible without the use of radioactive tracers. He pointed out that this new group of organic reagents will be useful for the purpose of improving the methods of separating and purifying radioactive tracers.

The last speaker of the session was S.T. Konobeevsky, Corr. Memb. Acad. Sci. USSR, who discussed the phase diagrams of some plutonium systems. He referred to methods that he had developed for the preparation of homogeneous alloys and for the metallographic, X-ray, thermal, and dilatometric study of metallic plutonium and its alloys on samples weighing from ten micrograms to tens or hundreds of milligrams. With the aid of these methods the phase diagrams of systems formed by plutonium with various metals were studied, and these studies enabled the speaker to establish certain regular features in the properties of alloys formed by plutonium with other elements.

Among those joining in the discussions on the papers were A.M. Zhirmunsky, Corr. Memb. Acad. Sci. White-Russian SSR, I.A. Kazarnovsky, Corr. Memb. Acad. Sci. USSR, Prof. P.I. Dolin, Prof. B.A. Dogadkin, S.Z. Roginsky, Corr. Memb. Acad. Sci. USSR, Academician A.N. Frumkin, V.I. Spitsyn, Corr. Memb. Acad. Sci. USSR, I.P. Alimarin, Corr. Memb. Acad. Sci. USSR, and Academician A.P. Vinogradov.

In a concluding address, Academician M.M. Dubinin surveyed the achievements of the three-day session in the three main sections of the program and drew attention to certain features of this conference. He pointed out that several very important problems of chemistry had been treated for the first time in lectures and discussions at a session of the Division of Chemical Sciences. It is regrettable, said M.M. Dubinin, that the limited time allotted to the program did not permit the inclusion of all of the papers submitted, and in this connection it might be added that a case could be made out for the systematic inclusion of papers on the use of atomic energy – both in purely chemical investigations, and also in technological processes – at sessions of the Division of Chemical Sciences.

Academician M.M. Dubinin referred to the interest taken in the proceedings of the session by the foreign guests, who had systematically attended all of the meetings. Soviet scientists – said M.M. Dubinin were glad to share the results of their investigations on the peaceful use of atomic energy and would welcome the further development of scientific contact between Soviet and foreign workers in all of the fields covered by the Division of Chemical Sciences. The most effective way in which such contacts can be made is by reciprocal visits to scientific institutes and by participation in joint scientific meetings. In conclusion, Academician M.M. Dubinin said that the interest taken by the Soviet chemical community in the meetings of this session was most graphically shown by the overflowing auditorium and the great activity of the participants.

After drawing attention to the substantial scientific achievements of the session of the Division of Chemical Sciences of the Academy of Sciences of the USSR on the peaceful uses of atomic energy, Academician M.M. Dubinin thanked all the speakers for the great trouble they had taken in the preparation of their papers and he thanked also the numerous participants of the session, who by their questions and discussions had helped to make it a success.

All the papers read at the session of the Division of Chemical Sciences of the USSR Academy of Sciences are included in the collected papers, published in Moscow (1955) under the title "Conference of the Academy of Sciences of the USSR on the Peaceful Uses of Atomic Energy, June 1-5, 1955".